SOME ASPECTS OF FREE RADICAL POLYMERISATION IN UV-CURING

BY

NERGIS ARSU

Supervisor: Professor R.S.Davidson

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Department of Chemistry
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To İSMAİL and ASENA

Her gün bir yerden göçmek ne iyi.
Her gün bir yere konmak ne güzel.
Bulanmadan, donmadan akmak ne hos.
Dünle beraber gitti cancağızım,
nekadar söz varsa düne ait.
Şimdi yeni şeyler söylemek lâzım.

MEVLÂNA (yenilestiren A.Kadir)

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ABSTRACT

Various quinoxalines,in association with N-methyldiethanolamine as synergist, were used to initiate the polymerisation of acrylates. It was found that the quinoxalines where used with amine synergist are efficient Type II initiators. It was also found that the cure of the acrylate is faster when oxygen is present in the reaction mixture than when it is absent.The photo-initiating efficiency of 2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one (IRG-907) was compared to different initiators using RTIR spectroscopy and N-Isopropylmorpholine(IPM) was used as a model to investigate the properties of the morpholino sustituent present in IRG-907. It was shown by RTIR spectroscopy, photocalorimetry,bulk polymerisation and the curing of thin films that IPM acts as a physical quencher for the triplet state of IRG-907 and that it is a very poor hydrogen donor.Sensitisation of IRG-907 by ITX was also investigated and it wasconfirmed that ITX can sensitise the -cleavage of IRG907. Photoinduced fragmentation of aminoalcohols by quinoxalines are discussed and the reactivity of the aminoalcohols reflect their ability to undergo electron transfer and to fragment.A wide range of aminoalcohols were synthesised and used as synergist in the polymerisation of a number of acrylates using different methods and the photoyellowing and photooxidation of aminoalcohols were also investigated.Some mixed acrylate-cinnamate systems were prepared to investigate a new dual cure system.The conversion percentage was found to be very low.The lack of cure is probably due to the cinnamates are scavenging the benzoyl radicals.

CHAPTER 1

GENERAL INTRODUCTION AND TECHNIQUES

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Chapter 1. GENERAL INTRODUCTION & TECHNIQUES

GENERAL INTRODUCTION

1. THE FUNDAMENTALS OF PHOTOCHEMISTRY

Although man was not present to observe the event, the first photochemical reaction occurred billions of years ago. High-energy solar radiation (λ <200 nm) undoubtedly was an important factor in the development of large molecules, polymers and eventually polypeptides from the primitive earth's reducing atmosphere (methane, ammonia and hydrogen). However, from man's point of view, the greatest photochemical "breakthrough" occurred when the first quanta of light were absorbed by a rudimentary photosynthetic unit, resulting in the release of molecular oxygen to the atmosphere, thus paving the way for all higher life:-

$$nH_2O + nCO_2 + \text{light absorber} \xrightarrow{h\nu} (CH_2O)n + nO_2$$

In 1912, one of the earliest photochemists, Giacomo Ciamician, realising the enormous potential of photochemistry, predicted "Solar energy is not evenly distributed over the surface of the earth: there are privileged regions, and others that are less favoured by the climate.... On the arid lands there will spring up industrial colonies without smoke stacks; a forest of glass tubes will extend over the plains and glass buildings will rise everywhere". Although the realisation of Ciamician's

prediction would be attractive in view of to-day's pollution-troubled industry, much of the recent rapid progress in photochemistry has arisen from the technological development of convenient and efficient high-intensity light sources, making dependence on the whims of the sun unnecessary.

The most important steps in photochemical reactions occur initially with the absorption of light energy emitted by a particular light source, followed by the conversion of the absorbing molecules into activated species. [1]

1.1 LIGHT ABSORPTION

Molecular excitation by light absorption takes place during the period of one vibration of the exciting light wave. For light with a wavelength λ equal to 300nm, this corresponds to 10^{-15} sec. This time period is too short for a change in geometry to occur. Hence the initially formed excited state must have the same geometry as the ground state. This is shown in Fig.1.1 for diatomic molecule.

The curves shown in this figure are called Morse curves and represent the relative energy of the diatomic system as a function of the distance between the nuclei of the atoms. For all points along the curve, the nuclei of the molecule are motionless, that is, the energy is completely potential.

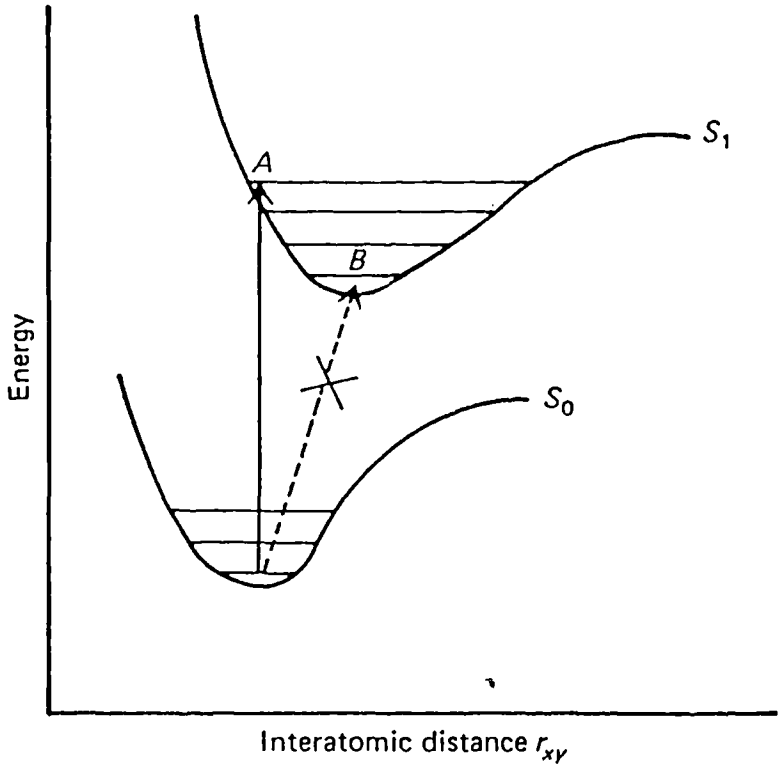


Fig. 1.1 Diatomic potential energy curves and Franck-Condon transition

The horizontal lines in the wells of these potential curves represent the vibrational levels of the states. According to the Franck-Condon principle, the time required for absorption of a photon is very small compared to the period of vibration of most molecules, which is of the order of 10^{-15} sec. Consequently, during the absorption process the nuclei do not alter their relative positions or their kinetic energies appreciably. This absorption of a photon does not exactly match the energy gap between ground and excited states and so usually produces a state which is excited rotationally and vibrationally, as well as electronically. In highly dilute gases, where collisional deactivation is slow, Franck-Condon excited states can actually be observed spectroscopically. However, in liquids and solids the

combination of a dense distribution of excited states and high collision frequencies between the molecules causes rapid relaxation of vibrational and rotational modes to occur very efficiently in about 10^{-11} sec, so that only molecules in the lowest vibrational level of the first excited electronic state persist long enough to be important photochemically. The energy associated with the absorbed light quanta is proportional to the frequency and is given by the following equation: [2-5]

$$E=h\nu=hc/\lambda=h\bar{c}\nu \qquad (1)$$

Where h=Planck's constant, c=velocity of light, ν=frequency and λ=wavelength of radiation.

In order to do quantitative photochemistry, one must know how much of the light incident upon a sample is absorbed. For most systems this can be conveniently determined using Beer's law $OD=\varepsilon cd$ [6]
Where the optical density OD is defined by:

$$OD = LOG(Io/I_t) \qquad (2)$$

ε is the molar absorptivity (also called the molar extinction coefficient), a constant characteristic for a specific wavelength of the molecule of interest, c is the molar concentration, d is the path length, Io is the

intensity of the incident light, and I_t is the intensity of the light transmitted through the sample. If the incident intensity is known, the absorbed intensity, I_a can be calculated since, thus from Beer's law:

$$I_a = I_o(1-e^{-2,3\varepsilon cd}) \qquad (3)$$

$$I_a = I_o - I_t \qquad (4)$$

The extinction coefficient has a cumulative property. For a mixture of two or more components, the extinction coefficient can be represented by equations(2-5).

$$\varepsilon = d(\varepsilon_1 c_1 + \varepsilon_2 c_2 + - - \varepsilon_n c_n) \qquad (5)$$

The quantitative relationship between the number of molecules which react or which are formed in a photochemical reaction and the number of photons absorbed in unit time is expressed by the quantum yield, Q. For a given system the quantum yield can be defined as follows:

$$Q = \frac{\text{number of molecules reacting in a particular process}}{\text{number of quanta absorbed by the system}}$$

A knowledge of the quantum yield is important for elucidating the reaction mechanism and the course of a photochemical

reaction. Thus when Q=1, every absorbed quantum produces one photochemical reaction; when Q<1, other processes compete with the main photochemical reaction; and when Q>1, a chain reaction takes place (3,5).

Energy Distribution in the Excited States

Photochemical reactions occur via electronically excited states, each excited state has a definite energy, structure and lifetime. The total energy of a molecule in a particular excited state is the sum of the electronic excitation energy (E_e), the vibrational energy (E_v), and the rotational energy (E_r) as shown in equation (6);

$$E=E_e + E_v + E_r \qquad (6)$$

where

$$E_e > E_v >> E_r \qquad (7)$$

The structure of various electronically excited states and the most important photochemical processes involved are represented in the Jablonski diagram (Fig. 1.2).

In this diagram the vertical direction corresponds to increasing energy. The electronic states are represented by the heavy horizontal lines; the symbols S_o, S_1 and S_2 represent the ground state and first and second excited

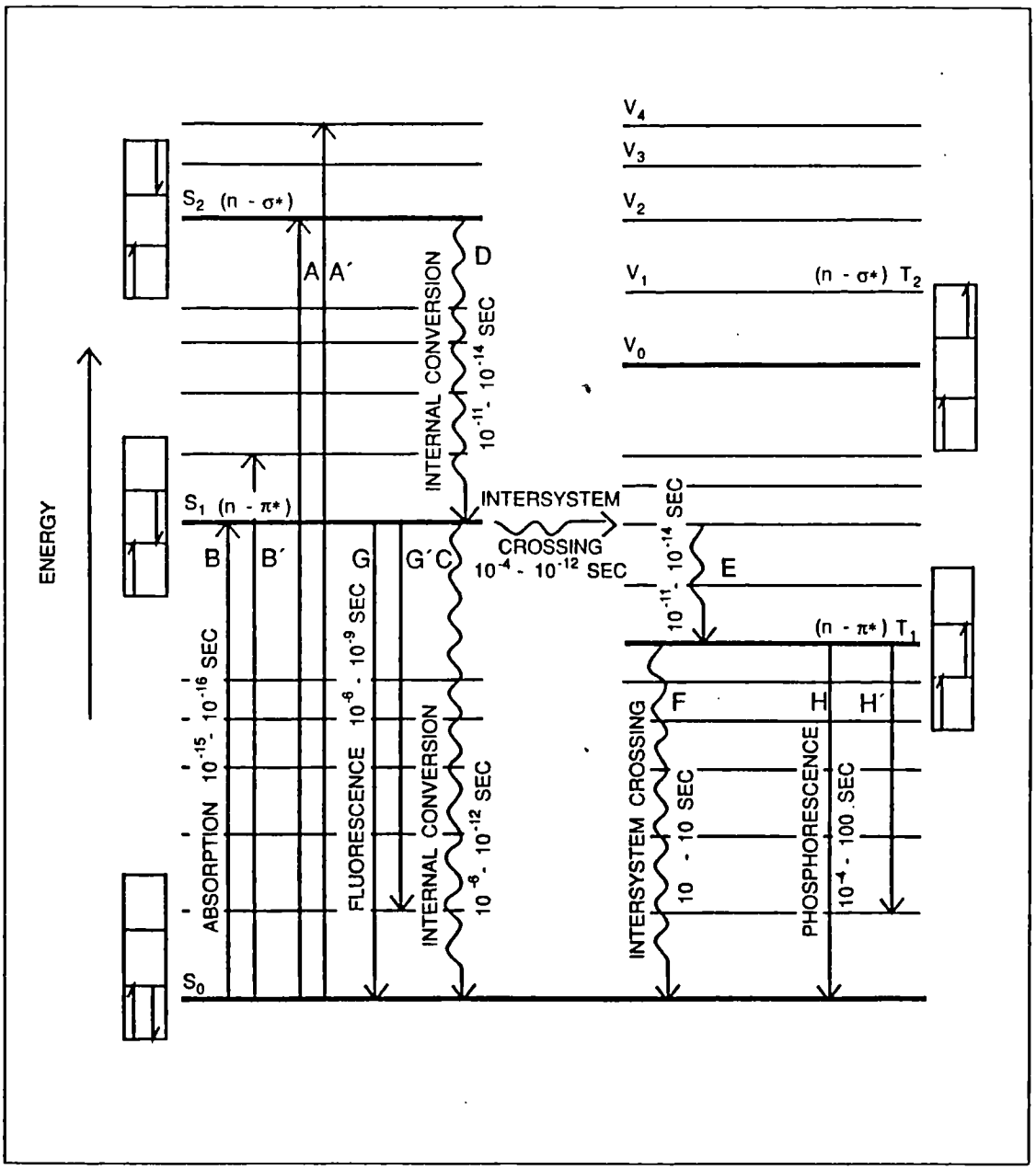


Fig.1.2 Jablonski Diagram for a Simple Carbonyl Compound (7)

singlet states, respectively, and T_1 and T_2 represent the triplet states. Excitation is represented by the promotion of one electron from the ground state (S_o) to a higher electronic level.

The position and spin of the excited electron relative to those of the electron in the ground state are noted in the boxes. Finally, the light horizontal lines correspond to the vibrational levels of the electronic states.

The lowest triplet level (T_1) is placed below the lowest excited singlet level (S_1), in accordance with Hund's rule, which states that the state of maximum multiplicity lies at the lowest energy. Since the two electrons having the same spin quantum number cannot be at the same place at the same time (Pauli exclusion principle), they will tend to avoid each other.

1.2 INTERNAL CONVERSION AND INTERSYSTEM CROSSING

After excitation has occurred, there are several processes which are important in the deactivation of the excited states. As shown in Fig. 1.1 a molecule undergoing a vertical transition upon excitation can arrive in the excited state with in internuclear distance (point A) considerably different from that corresponding to the minimum energy for the state (point B). In moving back to the equilibrium nuclear distance, the molecule finds itself three vibrational levels above its minimum energy. The excess vibrational energy can be dissipated via bimolecular collisions with solvent molecules. This process is called "vibrational relaxation" and is usually faster by several orders of magnitude than intramolecular processes involving transitions between electronic states. This means that most processes involving a change in electronic state take place from low vibrational levels. [1]

Internal Conversion is a non-radiative transition between states of like multiplicity:

$$S2 \longrightarrow S1$$

$$S1 \longrightarrow S0 \quad (K_{isc})$$

The conversion from Si to Sj is an isoenergetic process that is followed by vibrational relaxation of the new vibrationally hot state. A non-radiative transition between states of different multiplicity is called intersystem crossing:

$$S1 \longrightarrow T1 \ (Kisc)$$

$$T1 \longrightarrow So \ (Kd)$$

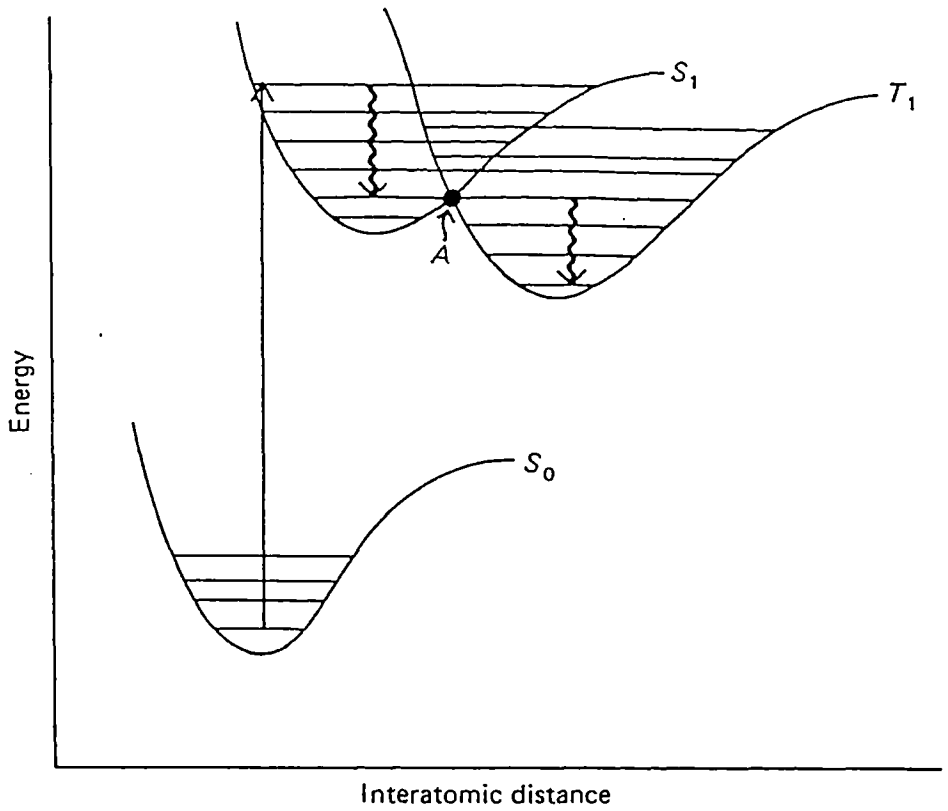


Fig. 1.3 Diatomic potential energy curves and intersystem crossing ($S_1 \rightarrow T_1$) at point A

Fig. 1.3 illustrates intersystem crossing as an isoenergetic process for a simple diatomic molecule. The crossing from the singlet to the triplet state has a maximum probability at point A in Fig. 1.3 where the energy and geometry of the two states are equal. Two important factors that influence the rate of the non-radiative process are:

(a) -Energy separation: the larger the energy gap, the slower the rate:

$$k(S2 \longrightarrow S1) > k(S1 \longrightarrow So)$$

(b) -Conservation of spin: transitions between states of different multiplicity are forbidden. However, these transitions can often compete very favourably with other processes:

$$k(S2 \longrightarrow) S1) > k(S1 \longrightarrow T1)$$

The ranges of the rate constants for these various processes for typical organic molecules are:[1,7]

$$k(S2 \longrightarrow S1) = \text{---} \; 10^{11}\text{-}10^{14} \; sec^{-1}$$
$$k(S1 \longrightarrow S0) = \text{---} \; 10^{5} \; \text{-}10^{8} \; sec^{-1}$$
$$k(S1 \longrightarrow T1) = \text{---} \; 10^{7} \; \text{-}10^{8} \; sec^{-1}$$
$$k(T1 \longrightarrow S0) = \text{---} \; 10^{-1}\text{-}10^{4} \; sec^{-1}$$

(c) -Fluorescence and Phosphoresence

These processes are radiative. Kasha's rule states that the light emitting level of a given multiplicity is the lowest excited level of that multiplicity. This is a reflection of the relatively large rate constants for the non-radiative processes S2 ⟶ S1 and S1 ⟶ T1 in comparison with those for S1⟶ S0 and T1⟶S0. Typical rate constants for radiative transitions between states of like multiplicity (fluorescence) and unlike multiplicity (phosphorescence) are in the following ranges:

$$kf = 10^{7}-10^{9}\ sec^{-1} \qquad kp = 10^{-1}-10^{4}\ sec^{-1}$$

the efficiency of these radiative processes often increases at low temperatures, or in solvents of high viscosity. The variation in efficiency of these processes as a function of temperature and viscosity of the medium indicates that collisional processes compete with radiative and unimolecular non-radiative processes for deactivation of the lowest singlet and triplet states.

1.3 PHOTOCHEMICAL KINETICS

For a molecule A undergoing light absorption and reaction in its lowest excited singlet state to form a product P, we can write the following hypothetical mechanism, where A^s and A^t are the lowest excited singlet and triplet state respectively.

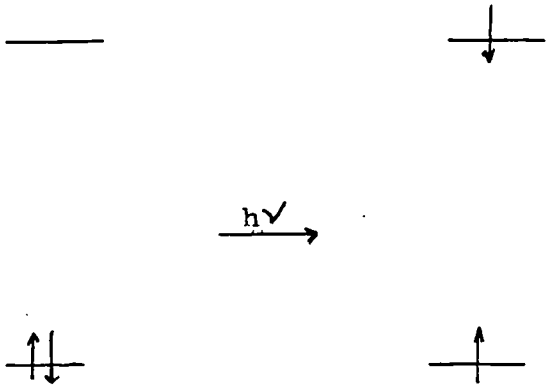
	Rate
$A + h\nu \longrightarrow A^s$	Ia
$A^s \longrightarrow A + h$	$(A^s)kf$
$A^s \longrightarrow A$	$(A^s)kic$
$A^s \longrightarrow A^t$	$(A^s)kisc$
$A^t \longrightarrow A + h$	$(A^t)kp$
$A^t \longrightarrow A$	$(A^t)kd$
$A^s \longrightarrow P$	$(A^s)kr$

For photochemical reactions and photophysical processes the efficiency determined by the quantum yield Q , which is defined as the number of molecules undergoing a particular process divided by the number of quanta of light absorbed.

1.4 CLASSIFICATION OF MOLECULAR ELECTRONIC TRANSITIONS AND EXCITED STATES

The physical and chemical properties of a molecule are determined primarily by the electron distribution in that molecule. Reactions that take place photochemically but not thermally result from the new electron distribution in the molecule resulting from excitation. The total energy is the result of electrostatic attractive interactions between nuclei and electrons, repulsive interactions between electrons and between nuclei and nuclei, vibration of the nuclear masses, molecular rotation and magnetic interactions resulting from spinning electrons and nuclei.

It is customary, to place electrons into the molecular orbitals and to consider light absorption as a one electron transition between the appropriate orbitals:



(a) $\pi \longrightarrow \pi^*$ Transitions

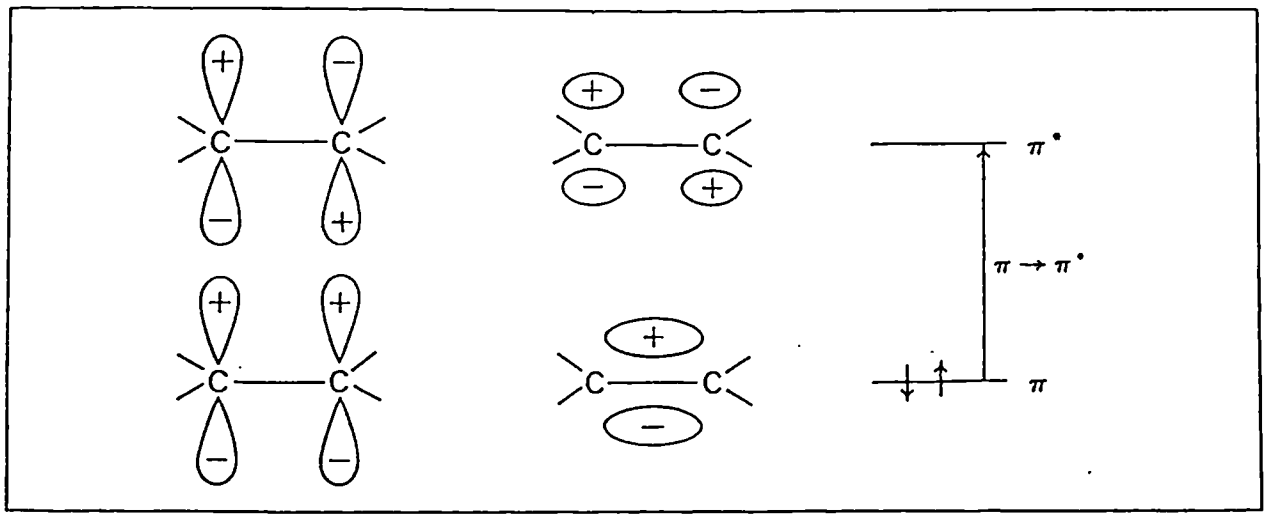


Fig. 1.4 The molecular orbitals of ethylene formed from the atomic p orbitals and the $\pi \longrightarrow \pi^*$ electronic transition.

In order for a transition to occur, the transition moment integral must be an even function. This integral is the product of the wave function corresponding to the ground state g an operator R, and the wave function of the excited state e. Fig. 1.5 shows all electronic transitions for the carbonyl group.

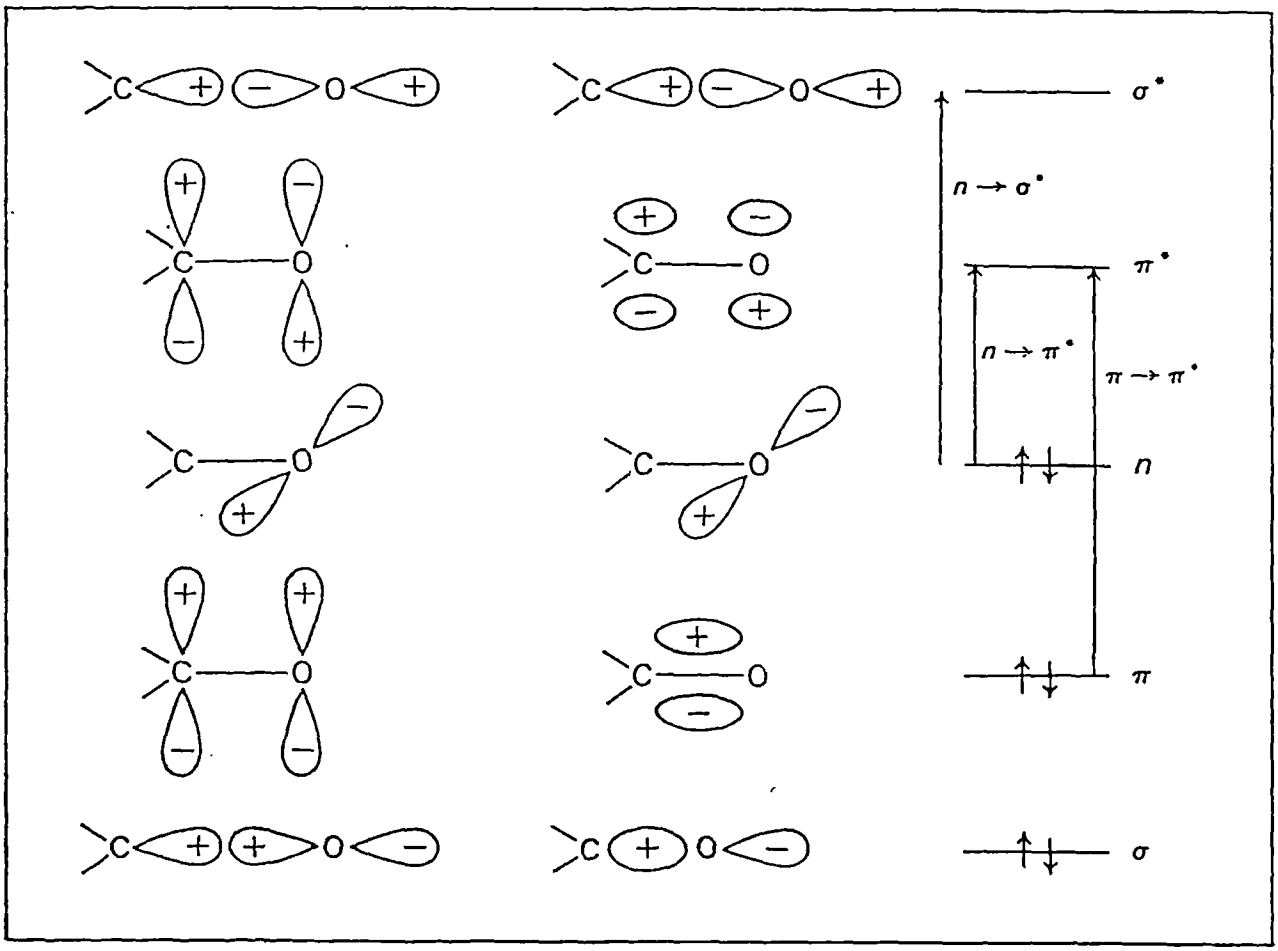
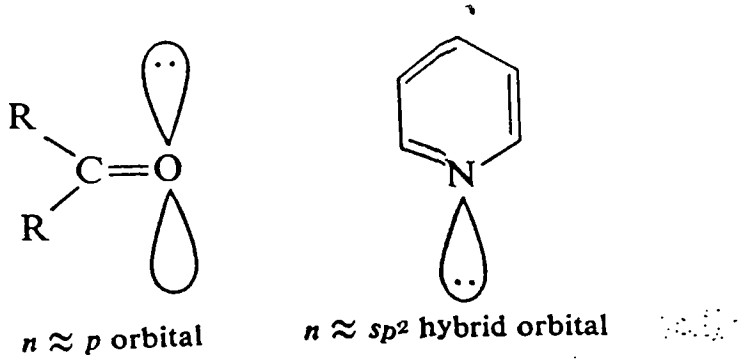


Fig. 1.5 Localised molecular orbitals formed from the atomic basic orbitals and electronic transitions for the carbonyl group

(b) $n \longrightarrow \pi^*$ Transitions

As Fig. 1.5 suggests, the lowest energy transitions for molecules with essentially non-bonding electron pairs is of $n \longrightarrow \pi^*$ character. These transitions are common for compounds containing oxygen, nitrogen and sulphur.



$n \approx p$ orbital $\quad$ $n \approx sp^2$ hybrid orbital

The $n \longrightarrow \pi^*$ transitions are weak (≈100l/mol.cm) since the lone pair does not overlap the space with the π system. Singlet - triplet splitting for $n \longrightarrow \pi^*$ excited states is small in comparison to that for $\pi \longrightarrow \pi^*$ states and an increase in solvent polarity produces a shift to shorter wavelength since in this case the excited state is less polar than the ground state. Since the energy separation between the singlet and triplet states is small, the rate constant for intersystem crossing is usually large.

2.0 PHOTOINITIATED POLYMERISATION

The photoinitiated polymerisation of unsaturated monomers can be controlled with more precision than thermally initiated polymerisation reactions. This is because the generation of the initiating species, which occurs through light absorption, can be varied by controlling the intensity of the initiating light.

UV radiation of short wavelengths will initiate the polymerisation of some unsaturated monomers directly. It is, however, general practice to use photochemical initiators which decompose rapidly into active species by UV light, thus initiating the polymerisation reaction much faster [8].

The photopolymerisation of the vinyl monomers can occur either by an addition or a condensation reaction. The photocondensation reaction is the least efficient of the two mechanisms [9 , 10]. It occurs by a step growth mechanism where the monomers first react with each other to form dimers which react to form tetramers and so on to give high polymers [9 , 10]. The most efficient and widely used reaction for the photopolymerisation of unsaturated monomers [11] occurs by an addition reaction. The addition reaction functions by a chain growth mechanism, where

monomer units add on to the growing end of a polymer chain. This efficient reaction mechanism can be controlled easily, but is susceptible to retardation and inhibition. The photoinduced species which initiate and generate the propagation of the chain include free radicals, anions or cations [3, 8]. The chain growth, or addition polymerisation mechanism is characterised by three main stages, which are the initiation, propagation and termination steps. All three steps differ significantly in rate and mechanism.

FREE RADICAL POLYMERISATION

The photoinduced free radical polymerisation reactions are used widely on a commercial scale for a number of different applications. High molecular weight polymers and copolymers are produced relatively easily with a number of different and specific properties. The final properties of the polymer film are obtained by the careful selection of specific monomers, prepolymers and oligomers from the wide variety available commercially. The three steps of a free radical polymerisation reaction are characteristic of all chain growth polymerisations [11].

INITIATION

The photogeneration of free radicals in the presence of vinyl monomer, results in the addition of the radical species to the double bond of the monomer. One electron from the double bond joins with the unpaired electron of the free radical to form a carbon-radical sigma bond. The other electron from the double bond moves on to the other carbon atom to generate a new radical centre. The addition of a free radical species to an unsymmetrically substituted alkene gives the most stable radical. The order of stability of radicals is like that of carbonium ions, i.e., tertiary > secondary > primary. If the photogenerated radical of the photoinitiator (PI) is designed by R·, then the first step in the reaction is the formation of the secondary radical [10]:

$$PI \xrightarrow{h\nu} 2R\cdot \qquad (8)$$

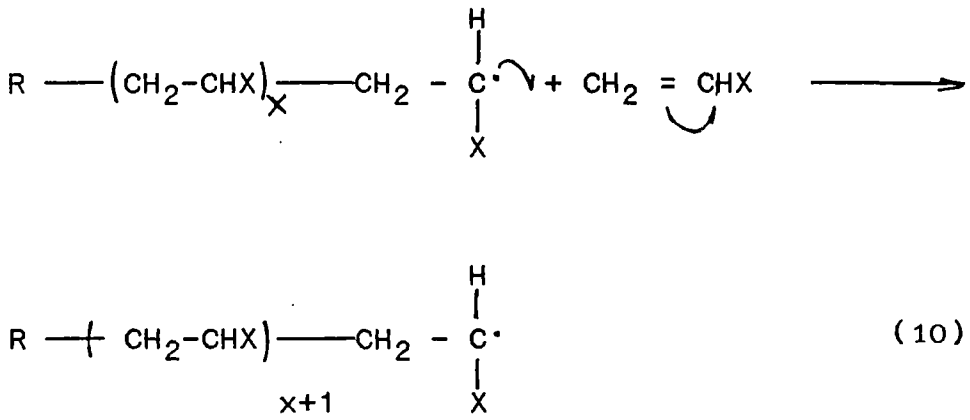
$$R\cdot + CH_2 = CHX \longrightarrow RCH_2 - \overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C\cdot}} \qquad (9)$$

The regeneration of another radical species is characteristic of chain reactions, which results in the

formation of a reactive growing end. Use of higher concentrations leads to shorter chain lengths (radical-radical combination). The concentration of photoinitiator used is generally low, (<5%).

PROPAGATION

The chain radical formed in the initiation step mentioned above is capable of adding successive monomers to its reactive growing end, i.e. at the radical centre, thus propagating the chain growth:



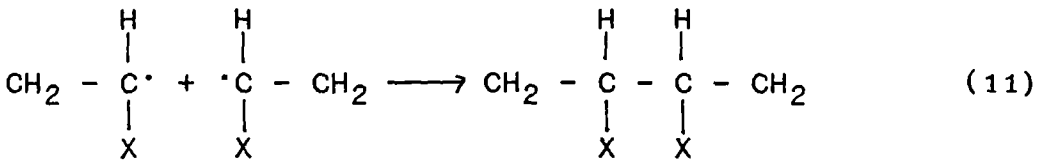
(10)

For chain addition reactions, the chain grows at the reactive growing end, the radical centre, only. [2, 8].

TERMINATION

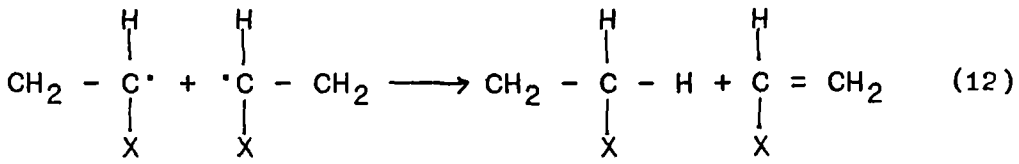
Theoretically, propagation would continue until the supply of monomer was totally exhausted. In practice however, in radical reactions, the growing chain is terminated, producing a stable polymer. The termination step can proceed via two mechanisms.

Termination by the formation of a covalent bond between the two radical species coming together, a process known as recombination or coupling, is merely the reverse of initiation.



(11)

Alternatively, termination can occur by disproportionation which involves the abstraction of a hydrogen atom from one radical species by the other radical species.



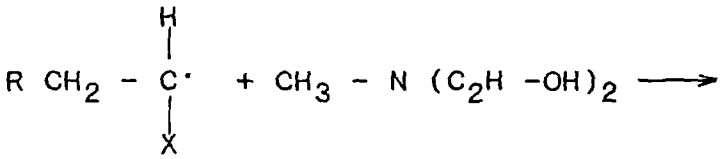
(12)

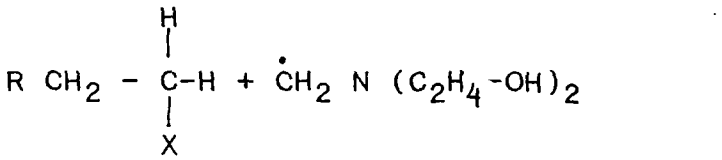
This hydrogen abstraction mechanism results in the formation of two molecules, one with a saturated and one with an unsaturated end group. [3, 8].

The three stages of polymerisation, initiation, propagation and termination are all necessary and have to be reasonably efficient to maintain a chain polymerisation reaction. Competitive reactions however can take place during the polymerisation.

The chain transfer reactions which occur during photopolymerisation, result in the transfer of the reactivity of the growing chain radical to another species capable of continuing the chain polymerisation reaction. Transfer may involve unreacted monomer or fully grown polymer, as well as solvent or 'chain transfer agent' if present.

An atom (usually hydrogen) is abstracted by the original radical, which dies in the process and a new radical is created at the site of abstraction. The following examples typify the transfer to solvent [13] , monomer [14] and polymer [15] respectively.





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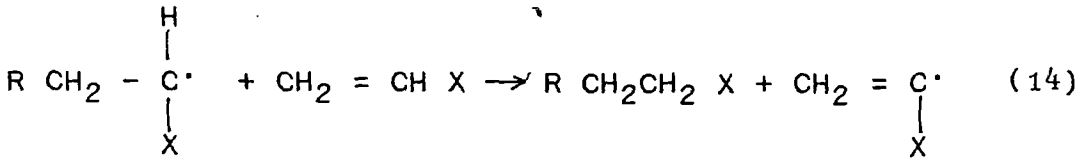

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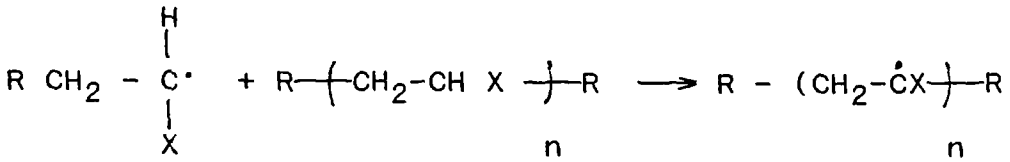
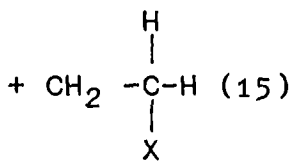




(15)

Chain transfer results in the formation of additional polymer molecules for each radical chain initiated. The transfer of radical reactivity to polymer and monomer with the subsequent polymerisation of the double bond can lead to the formation of branched molecules. The transfer does not

affect the overall rate of monomer consumption, but has a pronounced effect on the molecular weight distribution of the product.

The reaction of a radical with another molecule or substance which results in the formation of products incapable of adding to the monomer or the growing polymer chain is known as inhibition. If the inhibitor is very effective, polymerisation will be retarded, or even stopped altogether. In the majority of cases the action of an inhibitor is two fold. Initiators are capable of reducing the concentration of radical species, shortening their average lifetime and therefore the length of the growing polymer chain.

Oxygen inhibition is a significant problem encountered with the UV curing of unsaturated compounds in air. This matter is discussed in more detail in Chapter

PHOTOINITIATORS

Photoinitiators are classed into free radical and cationic and anionic. The free radical initiators are further subdivided:[7,15,16]

Type I : Photoinitiators which undergo cleavage to give radicals

Type II : Photoinitiators which require a synergist in order to produce radicals. Usually these materials are carbonyl compounds which undergo photoreduction e.g.:

$$Ar_2CO_{T1} + (RCH_2)_3\,N \longrightarrow Ar_2\dot{C}OH + R\dot{C}HN(CH_2R)_2 \quad \text{initiating radical} \qquad (16)$$

The photoinitiator should possess the following:-

(i) Good absorption characteristics for the cure system i.e. offer good light capture due to wavelength response and extinction coefficient.

(ii) The initiators should break down efficiently to yield the initiating species - ideally a quantum yield of 1 is desired.

(iii) The photogenerated species should react efficiently with the monomer.

(iv) The initiator should have adequate solubility in the prepolymer/polymer mix.

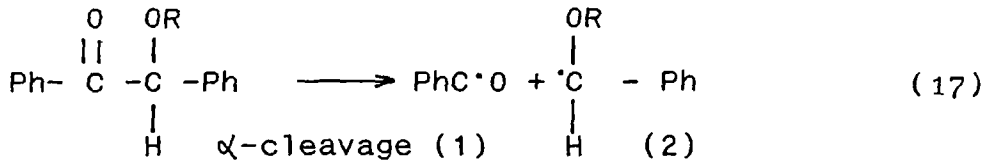
(v) The initiator should have a good storage stability including thermal stability.

(vi) The products of the photoreaction should not act as prodegradents for the film formed.

(vii) The photoinitiator and its breakdown products should not be toxic.

Free Radical - Type I Initiators

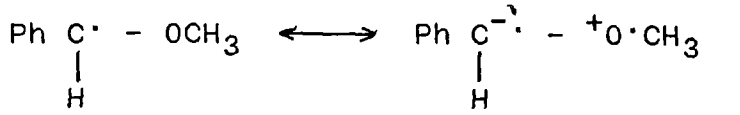
The initiators undergo fragmentation upon irradiation. Derivatives of benzoin were some of the earliest initiators to be introduced:



(17)

Clearly the carbonyl group is responsible for absorption of the radiation and as a consequence these compounds show a weak absorption band in the range 300-340nm which is associated with the n-π^* transition. Carbonyl compounds undergo intersystem crossing with high efficiency thereby populating the triplet state. The efficiency of this process appears to be unity. When R = alkyl the triplet states undergo rapid cleavage (k_r ~10^{10} sec^{-1}) whereas when R = acyl, cleavage is very much slower (k_r~10^6 sec^{-1}). This result implies that the energy of the radicals is

important, and although the triplet carbonyl has ~70 kcal/mol of energy available, the ∝-cleavage process is probably not exothermic. When R = alkyl the lone pair of electrons on the oxygen will stabilise radical (2) whereas with an acyl group the lone pair is conjugated with the carbonyl group. [17]



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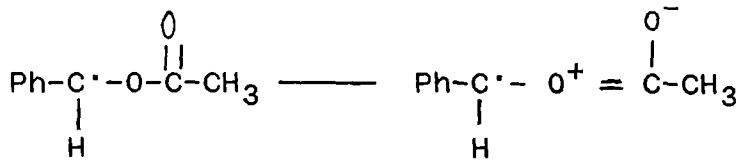
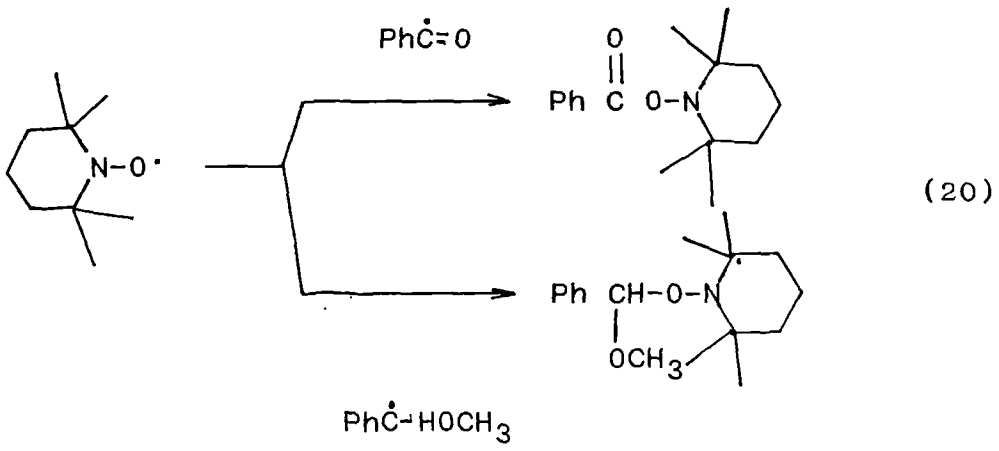


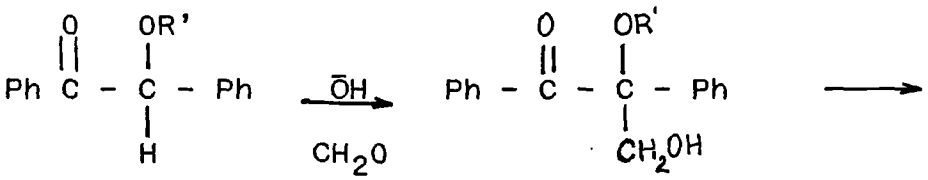
(19)

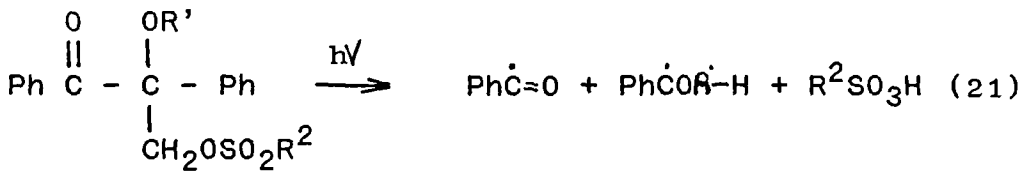
It has been demonstrated by end group analysis of the polymers formed that the benzoyl radical is responsible for initiating polymerisation of acylation. Radicals such as 2(R-CH_3) have been found to initiate the polymerisation of methyl methacrylate and so in principle benzyl methyl ethers offer the chance of producing two initiating radicals per photon absorbed. That irradiation of benzoin methyl ethers produces (1) and (2) has been demonstrated by radical trapping experiments.



(20)

These radicals can also be trapped by non-polymerisable olefins such as 1,1-diphenylethylene. The benzoin methyl ether has been modified to make acid generatable initiators, surfactant producing initiators and polymeric photoinitiators.

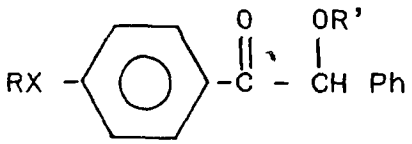




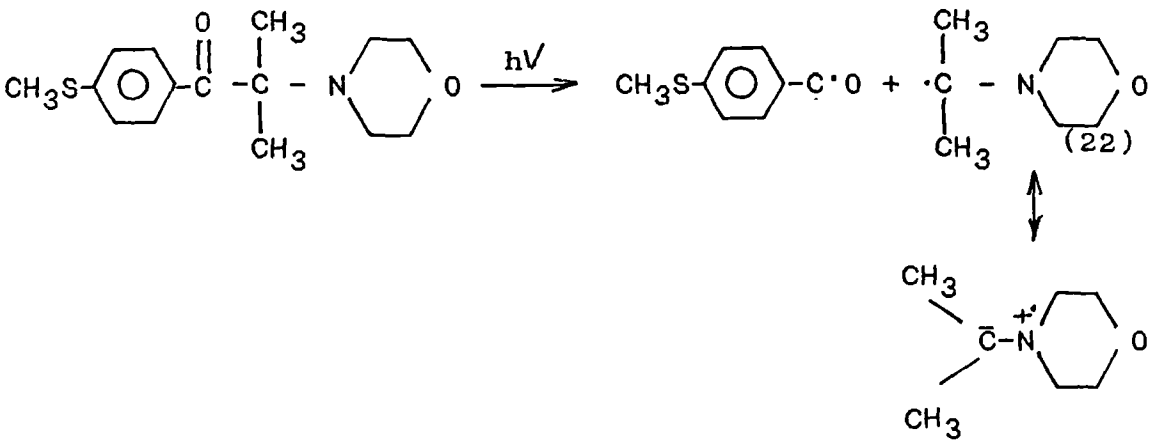
(21)

Although the benzoin methyl ethers undergo α-cleavage with

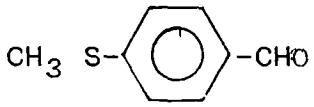
high efficiency and suffer little oxygen quenching of their excited states, they are of limited use because of their poor absorption characteristics which limits their use to clear varnishes (most pigments will screen the initiators). To move the absorption band further out to the red it is necessary to introduce electron donating groups.



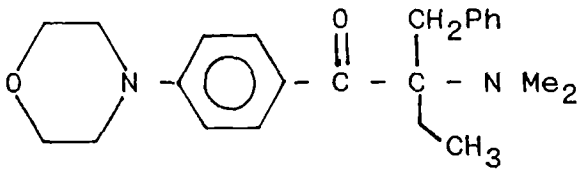
X=O has a small effect but that of X=S is far more striking. Introduction of these substituents does affect the electrons' properties in that the lowest excited triplet (in the case of S) becomes demonstrably a $\Pi\Pi^*$ triplet. The energy of this triplet is lower by about 10 kcal/mole. In order to get α-cleavage occurring with any degree of efficiency it is necessary to reduce the energy of the bond being broken and this has been achieved by replacing the alkoxy group with an amino group:[7,16]



The α-cleavage does not appear to be highly efficient and its rate constant has not as yet been determined. A drawback of these compounds is the production of sulphur-containing compounds e.g.:

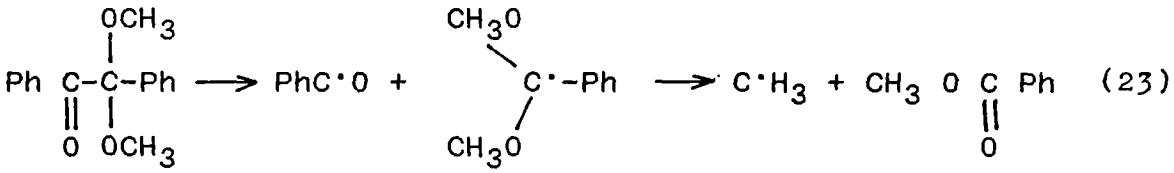


which impart an objectionable smell to the coatings. To overcome this problem and to increase the wavelength range for absorption, the following compound has been developed:[7,16,17]



This, like the sulphur-containing compounds, possesses a $\pi\pi^*$ triplet state.

A class of compounds closely related to the benzoin methyl ethers are the benzil ketals e.g.:



The α-cleavage reaction has a high rate constant ($\lesssim 10^{10} sec^{-1}$) and therefore the process suffers little from oxygen

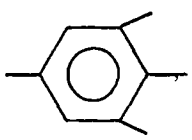
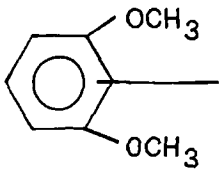
inhibition. That cleavage occurs in the manner shown has been demonstrated by esr spectroscopy, laser flash photolysis and radical trapping experiments. Use of these initiators has two disadvantages:

(a) production of methylbenzoate which imparts a smell to the coating and,

(b) clear films tend to photoyellow.

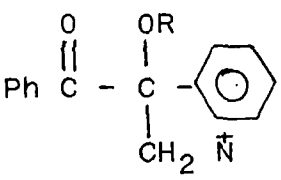
Acylphosphine oxides are a relatively new class of Type I photoinitiator

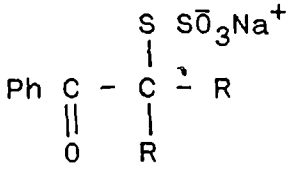
$$ArCOCl + Ph_2POMe \longrightarrow ArC(=O)P(=O)Ph_2 \xrightarrow{h\nu} ArC^{\bullet}O + Ph_2P^{\bullet}O \quad (24)$$

Ar =  or 

A particularly valuable feature of acylphosphine oxides is their strong absorption at ~380nm (10 2.7). This is undoubtedly due to a n π^* state. The long wavelength for absorption appears to be due to lone pair - lone pair interaction. The main use of acylphosphine oxides is in

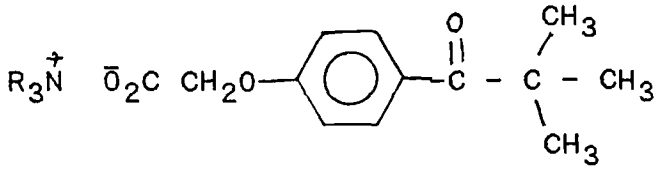
curing thick films and pigmented films. Curing is often slow due to the sensitivity of the system to oxygen inhibition. This latter effect renders acylphosphine oxides ineffectual for thin films unless amines are added which are the classic materials for reducing the inhibiting action of oxygen.





Water soluble Type I photoinitiators

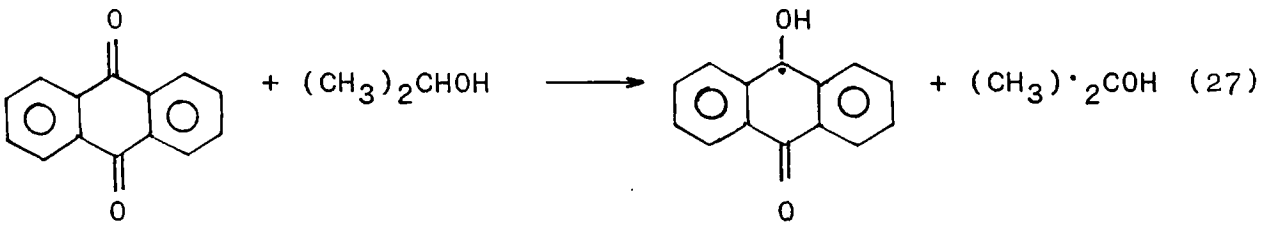
(25)



Type II Initiators

Many aromatic ketones possess $n\pi^*$ triplet states which have relatively long lifetimes (10^{-6} secs). A characteristic reaction of these compounds is H abstraction:[7,12,15,17]

e.g. $Ph_2CO_{T1} + (CH_3)_2\ CHOH \longrightarrow Ph_2C{\cdot}OH + (CH_3)_2\ C{\cdot}OH$ (26)



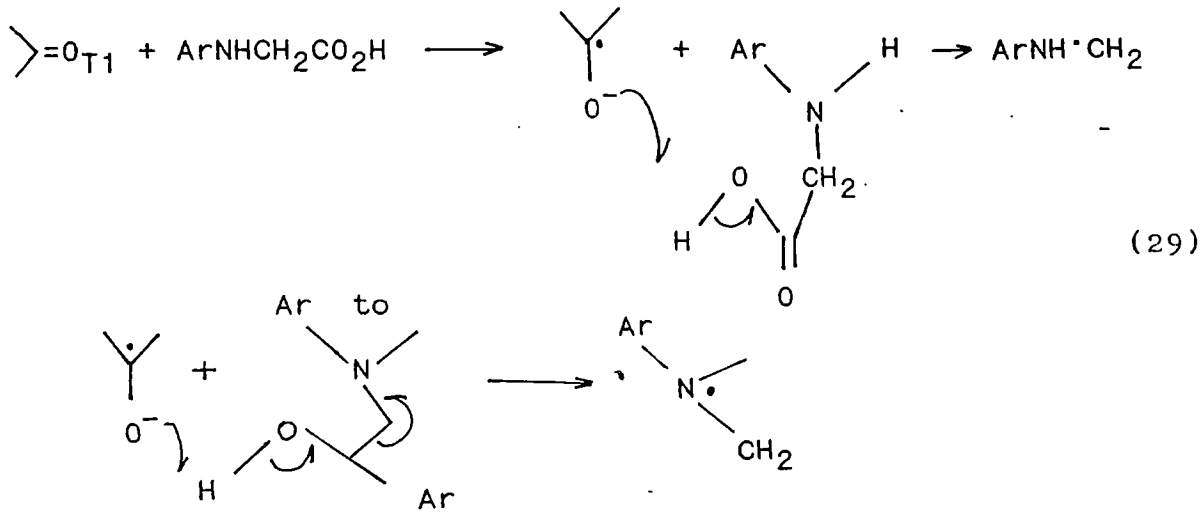
(27)

These reactions do not produce radicals which are capable of initiating polymerisation. However, when tertiary amines are used as the hydrogen donor, a potent initiating radical is generated. The amines are called "synergists".

$$Ph_2CO_{T1} + (RCH_2)_3\ N \longrightarrow Ph_2C{\cdot}OH + RC{\cdot}H\ N\ (CH_2R)_2 \quad (28)$$

The mechanism of this reaction has been the subject of a detailed examination and in general it appears to occur via ET and then H+. From this mechanistic study, developed the

concept of using aromatic amino acids and β-amino alcohols as synergists.



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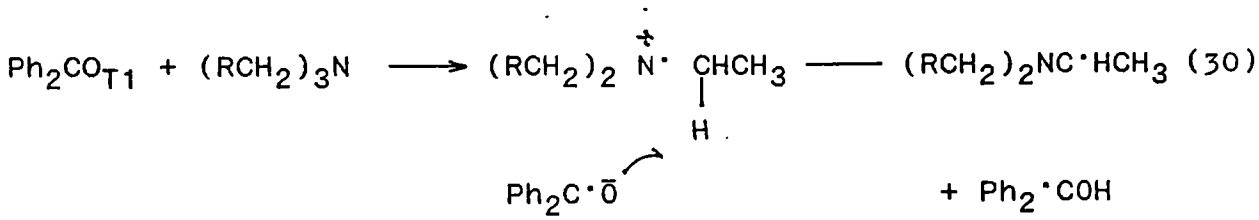

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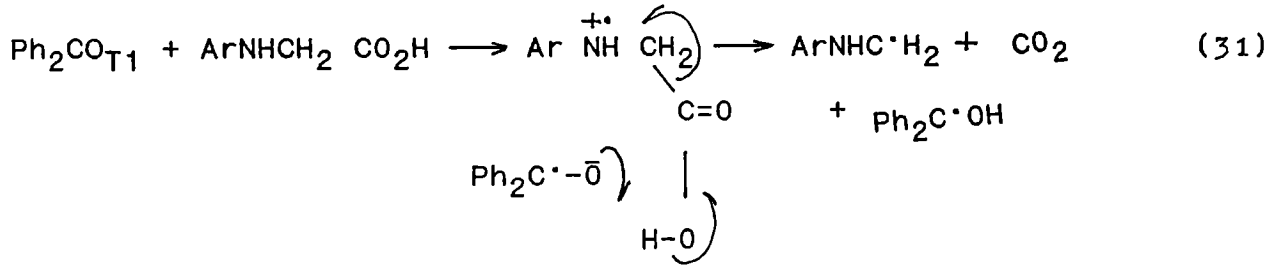


(31)

A particularly useful feature of the reaction of aromatic carbonyl compounds with tertiary amines is that reaction is also observed with carbonyl compounds which have triplet $\pi\pi^*$ states e.g. thioxanthones. A consequence of the carbonyl compounds having long triplet lifetimes is that they are very susceptible to oxygen quenching. The latter is diffusion controlled.

$$\frac{1}{T} = \frac{1}{T_o} + kq\,[O_2] \qquad (32)$$

$kq = 10^{10}$ $\quad [O_2] = 10^{-3}$

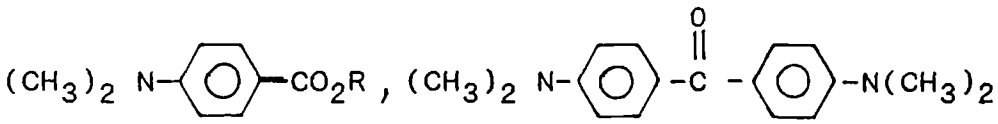
If $T_o = 10^{-6}$S lifetime reduced by $1/10^n$

i.e. lifetime has been cut down by 1/120 - 1/100, which will have a drastic effect upon the reaction with amine ($kr\text{-}10^9$ m^{-1} sec^{-1} [amine] $\sim 10^{-2}$).

Aromatic ketone triplets are quenched by electron acceptors and donors and acrylates, methacrylates. Styrenes etc. are quite efficient quenchers. In the case of styrene and N-vinyl-pyrrolidone quenching via energy transfer is so efficient that initiation of polymerisation of these systems by triplet carbonyl compounds cannot be carried out.

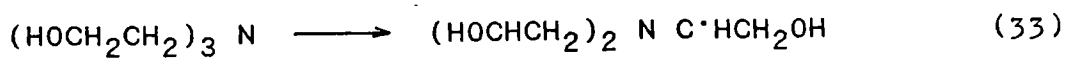
(a) Benzophenone This is the archetype and its chemistry has been well studied. The ketyl radical related to it, namely $Ph_2C^{\cdot}OH$, is not an initiator. Ph_2CO is reduced by a wide variety of amines. Strangely, the curing properties of Ph_2CO amine systems do not relate in a simple manner to the rate of reaction of Ph_2CO_{T1} and amine. Clearly, other factors are involved e.g. the ease with which the amine participates in chain transfer reactions. Some of the reactive amines commonly used are:-

$CH_3\ N\ (CH_2CH_2OH)_2$, $(CH_3)_2\ N\ CH_2CH_2\ OH$,



Michler's ketone

Amine radicals such as $C^{\cdot}H_2N(CH_2CH_2OH)_2$ have been shown to be powerful initiators. The polymers formed contain amines and this can have a deleterious effect upon the weatherability of the polymer.[18,19]



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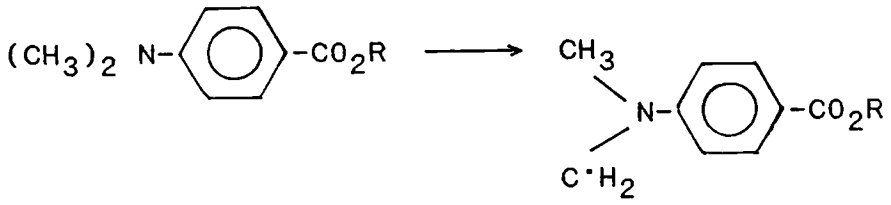

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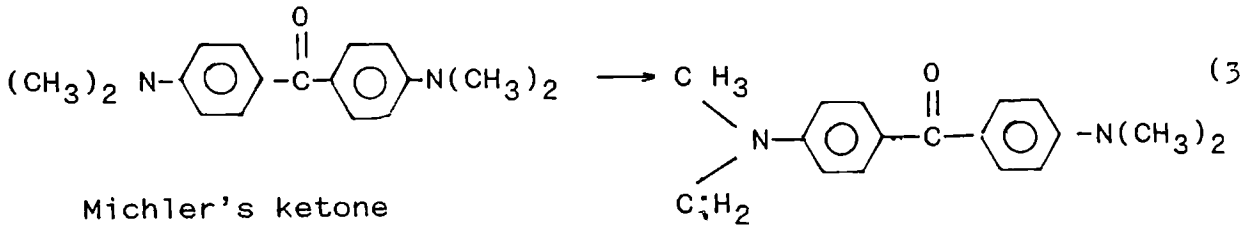
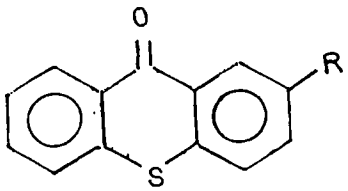


(35)

Michler's ketone



R = H, Cl or $CH(CH_3)_2$

Thioxanthone

(b) Thioxanthones

The main and very valuable feature of these compounds is their long wavelength absorption band (380-420nm log ~3.5-4.0) which enables them to be used in pigmented formulation (TiO_2). A number of water soluble thioxanthones are available.

(c) Aromatic 1,2-diketones

The simplest and most frequently used material is benzil and there is good evidence that this does not undergo ∝-cleavage on direct irradiation from its first excited triplet state.

$$\mathrm{Ph\,C(=O)-C(=O)-Ph} \xrightarrow{h\nu} 2\,\mathrm{PhC{\cdot}O} \qquad (36)$$

When benzil is irradiated in the presence of tertiary amines it is reduced to benzoin thereby generating initiating alkylamino radicals. The benzoin produced will also act as an initiator. Benzils show absorption around 350nm and are of some value for pigmented resins. Camphorquinone is used for visible light curing in dental formulations.

3.0 AMINES AS SYNERGISTS IN UV CURING

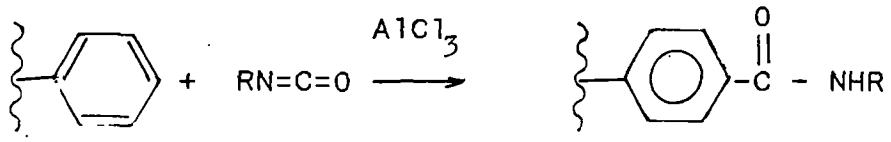
One of the two classical and well documented uses of amines is as a synergist for use with aromatic carbonyl compounds which do not undergo Type I cleavage. The subject has been thoroughly reviewed [12] and dealt with in a number of standard texts [4]. Tertiary amines are very potent hydrogen donors and are able to reduce carbonyl compounds having $n\pi^*$, $\pi\pi^*$ and ET excited states. When used in a UV curing system there is evidence to support the view that $\pi\pi^*$ are more reactive than $n\pi^*$ triplet states [20]. This at first sight is somewhat surprising when one considers that the $\pi\pi^*$ states are lower in energy than the $n\pi^*$ states [21, 22]. This is possibly the case since the energetics for the electron transfer process put the $\pi\pi^*$ states well out of the inverted region as defined by the Marcus Hush treatment for electron transfer processes.

Tertiary amines enable carbonyl compounds to be used as initiators which absorb in the region 300-400nm and which are normally unreactive towards hydrogen donors such as alcohols or ethers. Examples include anthraquinone [23], benzil [24], thioxanthones [25] and acylphosphonates [26]. A diketone which has attracted some attention is camphorquinone since in combination with an ester of 4-dimethylaminobenzoic acid it

provides a system that can be cured with light in the wavelength range of 350-450nm [27,28]. This system is now routinely used by the dental industry for capping teeth. Another excellent curing system which operates with visible light is based on the aminocoumarins and aminobiscoumarins [29]. The advent of water soluble benzophenones and thioxanthones [30,31] has helped to develop water compatible formulations and also emulsion polymerisation. In the latter system and ultrasonically dispersed acrylate/water mixture is circulated past a light source. Initiation of polymerisation can be carried out using a sodium benzophenone-4-methyl sulphonate in the presence of N-methyldiethanolamine or other water soluble amine [32]. Oil soluble amines are very ineffective in these systems thereby emphasising that initial radical production has taken place in the aqueous phase. An interesting development of substituted benzophenones is the linking of an alkyl amine to the nucleus thereby aiding intramolecular hydrogen abstraction [33].

Currently there is much interest in polymeric photoinitiators. These are perceived as having particular advantages such as reducing or eliminating the number of migratable species in the cured coating. Recently, 4-dimethylaminobenzophenone has been attached to a polystyrene backbone [34,35].

The initiators were prepared by taking polystyrene of defined molecular weight and then functionalised under controlled conditions.



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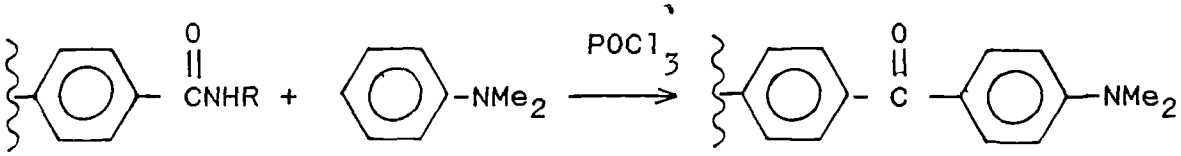


(38)

With these materials it was possible to show that under particular experimental conditions the aminoalkyl radical was acting as an initiating species. On the whole the reactivity of the polymeric initiator was lower than expected and this was attributed to inefficient energy transfer between the initiator molecules (due to self quenching) and the tendency to form light absorbing transients which give rise to an inner filter effect.

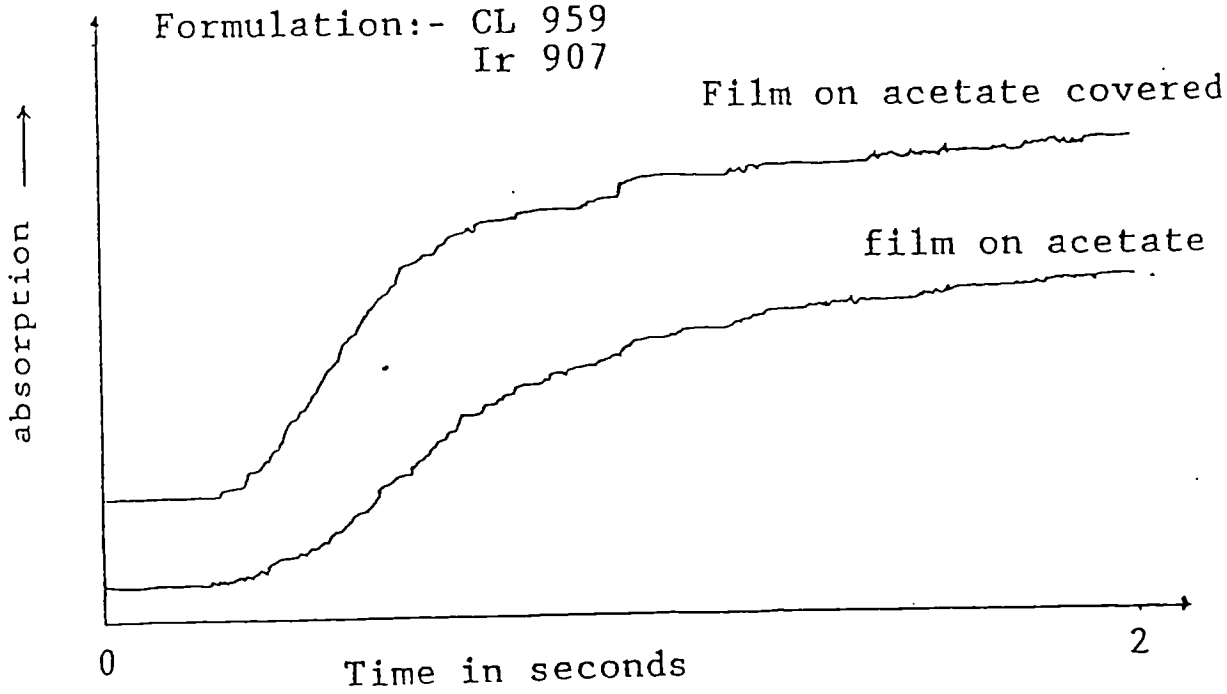
USE OF AMINES TO REDUCE THE EFFECT OF OXYGEN INHIBITION

Since virtually all UV curing systems are carried out with the coatings exposed to air, atmospheric oxygen is not only present in the film at the beginning of the cure, but it can also diffuse into the film during curing. The inhibiting effect becomes more pronounced the thinner the films become. When three dimensional objects are being coated, the applied diluent-oligomer mix is likely to be thinner along edges etc. and hence because of oxygen inhibition it can be difficult to get a uniform cure of the coating. The effect of oxygen inhibition upon cured flat coatings can often be detected by the surface of the film being tacky whereas the rest of the film is hard. Oxygen inhibits polymerisation by scavenging initiator radicals and the growing polymer radical i.e. usually carbon-centred radicals, whereas with Type II initiator systems it will (if concentrations are suitable) quench the triplet sensitiser by energy transfer. That oxygen can decrease the efficiency of Type I photoinitiators by scavenging the initiator radicals has been clearly demonstrated in a study upon acylphosphone oxides [36]. This type of initiator generates two initiating radicals - an acyl and a phosphinoyl radical. Both radicals are very effectively scavenged by oxygen which means that cure of thin

acrylate films by acylphosphine oxides requires the presence of tertiary amines [37,38]. Analysis of the reaction mixtures showed that the predominant role of the amines was that of an oxygen scavenger. A further piece of corroborative evidence [39] was that excellent cure could be obtained in the absence of amines provided a physical barrier (a polymer film) was placed directly on top of the acrylate mix thereby impeding the passage of atmospheric oxygen into the film.

Earlier work in which the oxygen concentration in the films was monitored clearly showed that amines serve to decrease the oxygen concentration in the film [40]. For the amines to be effective they have to be able to sustain the chain reaction involving reaction of α-aminoalkyl radicals with oxygen [41]. Thus it is not surprising to find that the structure of the amine has an effect upon the performance of amines in retarding oxygen inhibition [42]. Undoubtedly one of the most efficient amines is N-methyldiethanolamine.

The effect of oxygen inhibition upon cure can be readily detected by a number of techniques, such as kinetic analysis [43], differential scanning calorimetry [44], laser nephelometry and real time infrared spectroscopy [45]. The figure on the next page shows the curing of an acrylate with Irgacure 907 as initiator in the presence and absence of oxygen [46].



In all these experiments oxygen inhibition manifests itself by creating an induction period and reducing the rate of polymerisation.

4.0 HISTORY

One of the first examples known of a light-induced crosslinking-polymerisation dates back to over 4,000 years for the preparation of mummies. It is recorded that ancient Egyptians were dipping linen strips into bitumen of Judea which is known to contain unsaturated compounds, before exposing the swathed mummies to sunlight for hardening. They also employed this technology to seal ships with an asphalt-based oil that would polymerise upon solar exposure to give an impermeable and resistant coating. It was not until the early nineteenth century that Niepce had the bright idea to use a similar light-sensitive asphalt as an imaging material to obtain the first permanent photographic Scientific interest in UV curable systems developed only in the 1940s when the first patent was granted for unsaturated polyester styrene printing inks that polymerise readily under UV exposure.

During the last 25 years, an ever-growing number of resins that polymerise readily under UV radiations, in particular the very reactive multiacrylates, have appeared on the market when the many advantages of this new technology became apparent. Besides the quicker curing and lower energy consumption, when compared to conventional surface coatings, the major reason for the commercial breakthrough of UV curing

is its cost effectiveness, plus space saving, reduction of pollution and product quality. A large variety of monomers and oligomers are now commercially available which permits the production of a well-defined crosslinked polymer that will exhibit exact characteristics required for a particular end use.

Over the last decade, a considerable amount of work has been devoted to UV curing and has been recently reviewed in some comprehensive surveys [4,15,47-51].

Photopolymerisable Resin Systems

Prepolymers

Over the last 15 years or so, the surface coatings industry has seen a rapid growth in the tonnage of UV curable media used. The increase in the number of different applications has led to the development of a variety of novel UV curable resins. The solvent free, 100% solid photopolymerisable resins used in numerous industrial applications contain a substantial amount, up to 58%, of a mixture consisting of a reactive viscous prepolymer or oligomer and mono - or polyfunctional monomer acts as a reactive diluent of low viscosity and is co-polymerisable with the prepolymer [2 - 4, 49,52]. During the development of a UV curable formulation the primary objective involves the selection of, or the

design and synthesis of a polymer (prepolymer or oligomer) which will impart the optimum properties for the proposed application of the surface coating. Such properties are most likely to include adhesion to a variety of substrates, tensile strength and flexibility. The prepolymer must also have good pigment wetting and rheological properties. Currently, the polymers found to meet these requirements include unsaturated polyesters, epoxyacrylates, polyester acrylates, urethane acrylates and polyether acrylates.

Unsaturated Polyesters

The earliest types of resins used in UV curing systems involved unsaturated polyesters dissolved in styrene and other monomers (i.e. butane-1,4-diol). These systems were mainly used, and still are, for wood finishing, as fillers, sealers and lacquers. Despite their good mechanical properties and significant cost advantage, the general properties of the unsaturated polyesters are inferior to the current systems available. Unsaturated polyesters are characterised by slow curing properties, insufficient adhesion and flexibility on metals, plastic foils and paper, and a concomitant volatile, low flash point solvent (styrene) [2-4,49,53].

Polyester Acrylates

Although these compounds are polymers, their characteristic low viscosity enables polyester acrylates to be used as reactive diluents. The preparation of polyester acrylates involves either the synthesis of a saturated polyester backbone with residual hydroxyl groups which are then esterified with acrylic acid, or by reaction of an unsaturated primary alcohol, such as a hydroxy acrylate with residual acid groups on the polyester chain [2-4,53]. Both preparations result in acrylate groups attached to the polyester backbone. As mentioned, radiation curable polymers are characterised by their low viscosity and their relatively low cost compared with other acrylated polymers.

The advantageous properties of the films formed from these resins leads to them being used as overprint varnishes for polyurethanes, PVC, leather, metals, and so on.

Polyether Acrylates

Polyethers are another class of low molecular weight, low viscosity resins, which can be acrylated to produce relatively inexpensive polyether acrylate polymers. The polyether acrylates tend to yield very hard films with low flexibility and for this reason are not recommended for

coating metals, plastics and paper. However, a new generation of low viscosity, low toxicity polyether acrylates, such as the ethoxylates and propoxylates of trimethylolpropene, pentaerythritol and polyethers of butanediol have been used in a large number of applications [2-4,53].

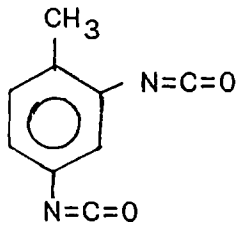
Acrylated Epoxy Resins

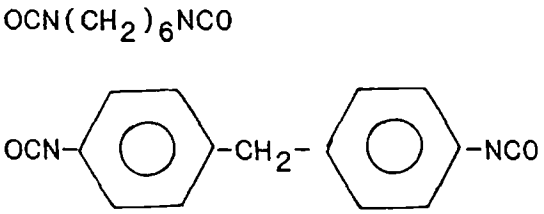
The mechanical and adhesive properties of epoxy acrylate UV curable resins are much better than those of similarly cross-linked polyester resins. There are a number of epoxy containing compounds which can be acrylated, including the bisphenol A diglycidyl ethers, epoxidised oils and epoxy novalacs.

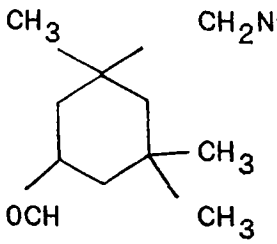
Epoxy acrylates are noted for their adhesion to many different substrates, flexibility, high level of chemical resistance and non-yellowing properties. Due to their highly viscous nature, considerable amounts of reactive diluents of low viscosity polymers need to be added in order to obtain a satisfactory application viscosity. Despite this, the versatility of epoxy acrylate polymers enables their use in a number of different UV curable applications, including coatings for metal, paper, board, and wood, as well as inks [3,4,15,53,54].

Urethane Acrylates

Urethane acrylates are formed by reaction of multifunctional isocyanates with a functionalised acrylate e.g. 2-hydroxyethylacrylate, 2-hydroxypropyl acrylate. The isocyanates used are shown below:







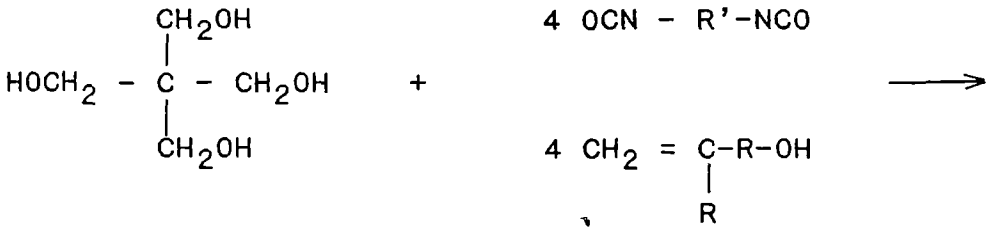
Isoborana isocycanate

$$CH_2 = CHCO_2CH_2CH_2OH + O = C = N - R - N = C = O \longrightarrow \quad (39)$$

$$CH_2 = CHCO_2CH_2CH_2OC(=O)\,NH - R - NHC(=O)\,OCH_2CH_2OC(=O) - CH{=}CH_2$$

Flexibility can be introduced into the film by reacting the diisocyanate with a polyethylene glycol together with the 2-hydroxyethylacrylate. As flexibility increases, hardness, speed of cure and solvent resistance decreases.

Reaction of diisocyanates with polyols and hydroxyethyl-acrylates gives highly branched structure thereby leading to highly crosslinked films.



(40)

Urethane acrylates are fast curing but expensive. They are often used in conjunction with other prepolymers.

Diluents

Diluents for use in radiation curable systems can be classed as nonreactive and reactive diluents. They form an extremely important part of radiation curable formulations

since they control the viscosity. Reactive diluents contain at least one double bond for copolymerisation by a free radical mechanism.

Reactive diluents are added to viscous prepolymers to modify viscosity, tack and properties of the cured film such as flexibility and hardness. Reactive diluents can be classified as monofunctional & multifunctional diluents.

Monomers

The monomers are classed as mono, di, tri etc. functional species. Monoacrylates can only give linear chains whereas the others, via crosslinking, can produce a network. Low viscosity and good solubility are clearly desirable features. The volatility flashpoint and odour, are particularly important considerations in the choice of monofunctional monomers. Other factors are Tg (glass transition temperature) of the homopolymer and extent of shrinkage upon cure.

Monofunctional Monomers

A wide selection of monofunctional products is available, such as styrene, vinyl toluene, vinyl acetate and N-vinyl pyrrolidone. Both styrene and vinyl toluene are slow curing. Vinyl acetate is very reactive but is also very volatile and has a low flashpoint. NVP is a very useful

monofunctional monomer. This is due to its excellent viscosity cutting properties and high reactivity.

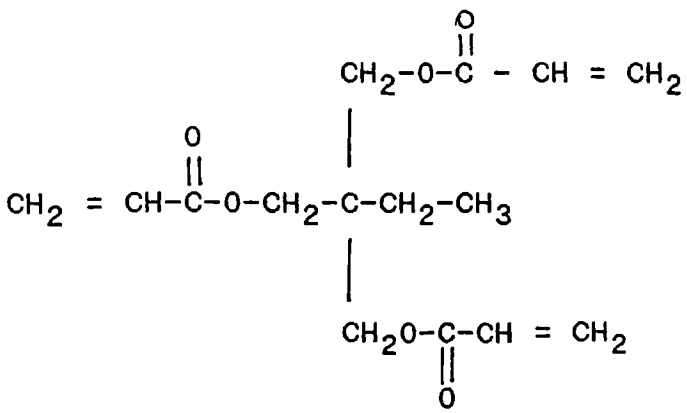
Difunctional Monomers

These are produced by transesterification of methyl acrylate with a diol. Over the past 20 years of the development of radiation curable materials, a wide selection of diols has been used, e.g. ethylene glycol, diethylene glycol and triethylene glycol.

Trifunctional Monomers

These are usually considerably higher in viscosity, and have higher reactivity than the difunctional acrylates. They contribute hardness and to some degree brittleness to the final coating.

Trimethylol propane triacrylate.



TMPTA has a viscosity of around 100cps and has a high reactivity.

GENERATION OF ULTRAVIOLET RADIATION

There are almost as many sources of ultraviolet energy as there are applications for its use. Ultraviolet light is not a single entity but is a very wide band of wavelengths. Therefore the efficiency of an ultraviolet source must be considered in terms of the power produced at wavelengths compatible with the absorption spectrum of the initiator system. For most materials used for UV curing, these are generally accepted to be between 200 and 400 nanometres with peak absorption at around 365nm. During the selection of the UV light source for the photo-polymerisation of UV curable formulations, certain characteristics need to be considered. These are a high intensity in the desired spectral region, long life, stability of output, ease of operation, proper physical dimensions for the process under consideration, and the minimum amount of ancillary equipment.

The most common source of UV used for coatings and inks is the mercury vapour lamp [2-4]. Mercury vapour lamps are available at low, medium and high pressure.

Low-Pressure Lamps

The least expensive and most efficient of all mercury vapour lamps is the low pressure or germicidal lamp. It operates at pressures in the 10^{-2} to 10^{-3} Torr region and at relatively low temperatures ($40^{o}C$).

Low and medium pressure mercury lamps are constructed of a quartz envelope which is evacuated of air and sealed at the ends.

-They are partially filled with argon or xenon as a starting gas and dosed with a small amount of mercury[2].

-Electrodes are located at either end of the tube and an arc is struck by passing an electric current between the electrodes. The vapourisation and ionisation of mercury atoms occurs through collisions with electrons of sufficient kinetic energy, as shown in Scheme 1.

Scheme I

$$e + Hg \longrightarrow Hg^{*} + e$$

$$Hg^{*} + e \longrightarrow Hg^{+} + 2e$$

$$Hg^{*} + Hg^{*} \longrightarrow Hg_2^{*} + e$$

$$Hg^{*} + Hg^{*} \longrightarrow Hg^{+} + Hg + e$$

The excited mercury electrons move from one transition state to another, lower transition state, energy is released as photons. The wavelength emitted by the photon depends upon the actual transition taking place.

The UV output of low pressure lamps is very efficient, the intensity is very low which can result in the limited penetration of the short wave UV through the surface coating, and therefore longer curing times. Low pressure lamps do not find wide application in UV curing appliances, in spite of a number of advantages e.g. low cost, long lifetimes.

Medium-Pressure Mercury Lamps

Medium-pressure mercury lamps are the most widely used lamps for UV ink drying and the curing of coatings. They have a much higher power output than the low pressure lamp, running between 40 and 120 watts/cm linear lamp length with pressures of 10^2 Torr. The tube is constructed of

transparent quartz and runs at a surface temperature of 700°C. The MP Hg lamp needs to be cooled to control the temperature which, in turn, helps to maintain a steady spectral output. The use of an appropriate extraction unit to cool the lamps will also serve to remove any ozone produced.

Compared with low pressure lamps, the 253.7nm line is relatively insignificant, but 365nm or 366.3 nm. lines are very prominent and important in the UV curing process. The lifetime of these lamps is guaranteed to be about 1,000 hours, although 2,000 hours may be a more realistic figure [2]. The medium pressure mercury lamps emit 17.4% UV from the 200-400nm region, 23.8% of visible light, 5.8% infrared radiation, and 53% of their input power is lost as heat.

High-Pressure Mercury Lamps

High-pressure mercury vapour lamps, operate above 10 atmospheres and contain a mixture of mercury and xenon. The light output is about ten times that of a medium-pressure mercury lamp and 100 times that of a low-pressure lamp.

The lamps are usually smaller in dimension than the medium-pressure mercury lamp and find applications in photolithography [2-4].

POTENTIAL HAZARDS OF AN ULTRAVIOLET SYSTEM

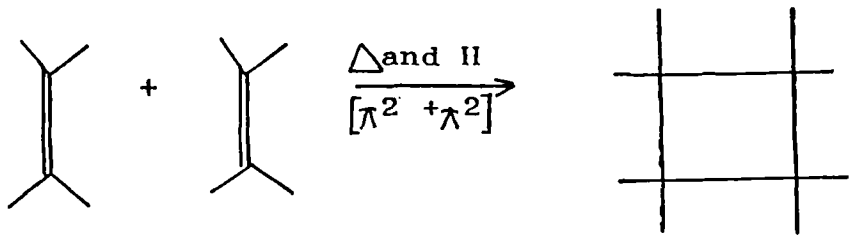
Although the use of acrylate monomers in UV curable formulations imparts a wide range of property advantages, the associated hazards of handling these materials have probably been one of the main reasons why the growth of the UV curing industry has not been much greater. The most serious hazards include the toxicity of the monomers and photoinitiators. During the handling of these materials care must be taken to avoid both skin and eye contact, as well as inhalation, which could damage the respiratory tract.

In the case of stray UV light, the emitted radiation at wavelengths of 254nm can severely affect the eyes and skin. Observing an unscreened mercury arc at several metres distance is sufficient to cause painful eye conditions and also to cause burning of the skin. The formation of ozone occurs as the short wave UV (i.e. below 220nm) passes through air. It is important to avoid the build up of toxic ozone concentrations, hence adequate ventilation is required. However, the formation of ozone can be eliminated using quartz or Pyrex screens to absorb the short wave UV radiation.

Introduction to [2 + 2] Cyclo-addition Reactions

Cyclo-addition reactions are of considerable importance in synthetic organic chemistry. In a cyclo-addition reaction, two sigma bonds are formed to give a new ring structure derived from each of the reacting units [55]. The rationalisation of concerted reactions, by Woodward and Hoffman [56,57] in terms of the conservation of orbital symmetry during the course of the reaction, has given insight into thermal and photochemical cyclo-additions. Cyclo-addition reactions are not all concerted and may proceed via a variety of distinguishable routes.

One of the simplest classes are [2 + 2] cyclo - additions (Eq. 41) . such as the reaction of two alkenes to form a cyclobutane ring. It occurs under both thermal and photochemical conditions.



(41)

The planes of the two ethylene molecules are assumed to be parallel as they approach each other, the cyclo-addition reaction is suprafacial to each component and may be represented formally as a [π2s + π2s] process Fig. (1.6).

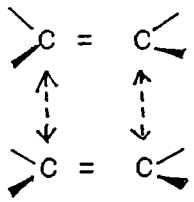
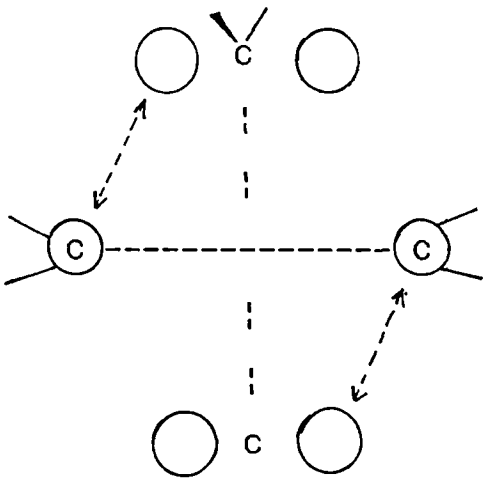


Fig. 1.6 $[\pi 2_s + \pi 2_s]$ cyclo-addition

-An alternative course for this reaction occurs when the ethylenes approach in orthogonal planes. This involves addition to one component in a suprafacial manner and to the other component in an antarafacial manner.



(1)

Fig. 1.7 $[\pi 2_s + \pi 2_a]$ cyclo-addition

Thus the cyclo-addition (1) can be described as a $[\pi 2_s + \pi 2_a]$ process where the molecule drawn vertically undergoes antarafacial addition and the other molecule (drawn horizontally) suprafacial addition.

5.0 TECHNIQUES

Real-Time Infrared (RTIR) Spectroscopy

The light-induced polymerisation of multifunctional monomers has found widespread applications in various industrial sectors, in particular for the surface protection of organic materials by UV curable coatings, the manufacture of optical lenses and video disks, as well as the production of fast hardening composites and adhesives. Various analytical methods have been employed to study the kinetics of these ultra-fast reacting systems, such as DSC [58], IR spectroscopy [59,60], laser nephelometry [61], interferometry [62], dilatometry [63,64], etc.

The RTIR method has proved extremely valuable for measuring the polymerisation rates and quantum yields of reactions that develop in the millisecond time scale [60,65]. The basic principle of this method of kinetic analysis consists in exposing the sample simultaneously to the UV beam which monitors the resulting drop in the absorbance of the reactive double bond. The IR spectrophotometer must be set in the absorbance mode and the detection wavelength fixed at a value where the monomer double bond exhibits a discrete and intense absorption for acrylic monomers (CH = CH_2 twisting).

During UV exposure the intensity of the absorption at 810 cm^{-1} is continuously monitored and this reflects the fast decrease of the 810 cm^{-1} peak.This will accurately reflect the extent of the polymerisation process since the absorbance increment $(A_{810})_0-(A_{810})_+$ is directly proportional to the number of acrylate functions which have polymerised.

Following continuously the variation of the IR signal intensity in this way allows conversion versus time curves to be directly recorded for polymerisation developing on a time scale of less than 15 secs.

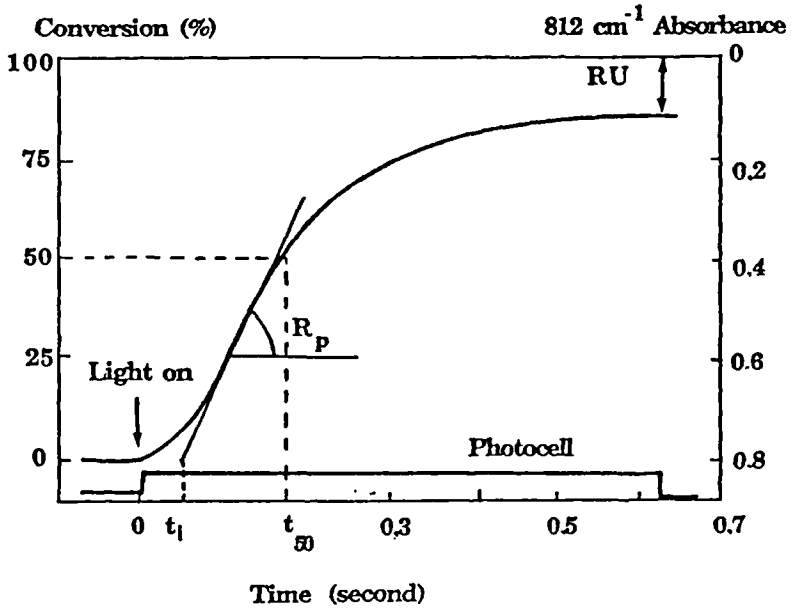


Fig.1.8 shows a typical polymerisation profile recorded by RTIR spectroscopy for an acrylic monomer (Acticryl CL 960) in the presence of air.

One of the distinct advantages of RTIR spectroscopy is that the most important kinetic parameters of a photopolymerisation can be evaluated in a single experiment: the rate of the reaction, the quantum yield of polymerisation, the induction period, the photosensitivity, and the residual unsaturation content of the polymer formed.

Advantages and Limitations of RTIR Spectroscopy

This technique offers several advantages and disadvantages.

Real-time monitoring: Cure reactions occurring in a fraction of a second can now be followed continuously from the very beginning of the process to its end, thus providing a precise analysis of the quasi-instant liquid-solid phase change.

High light-intensity operations: RTIR spectroscopy permits the study of kinetics of cure reactions over a very broad range of light intensity, in particular those performed under intense illumination and in the presence of air, i.e., experimental conditions very similar to those found in most industrial UV curing operations.

Quantitative results: RTIR spectroscopy is the first technique to provide in real time quantitative information

about the important kinetic parameters: induction period, polymerisation rate, photosensitivity, residual unsaturation of tack-free and scratch-free coatings.

Practical advantages: Since it is based on IR spectroscopy, the RTIR technique proved to be both reliable and highly sensitive, leading to accurate and reproductible results. In addition, it offers some valuable advantages such as speed of analysis, ease of use and low cost, for it requires only a routine IR spectrophotometer.

Assessments of Properties: The cured coating can be examined at any moment of the reaction for evaluation of some of its physical characteristics, such as hardness, abrasion resistance, flexibility, solvent resistance, gloss, heat resistance, etc...

Versatility: A wide range of applications can be examined by this novel technique of kinetic investigation, since essentially any fast polymerising system, clear or pigmented, can be analysed in real-time. It can be extended to other types of radiation such as lasers, microwaves and electron beams.

Disadvantages: These are respectively:-

- Vulnerable to phase/baseline changes
- Sample must be either viscous or enclosed (machine dependent)

- Response speed limited by mechanics and electronics of the spectrophotometer (machine dependent)

Comparison with other analytical methods

The performance of RTIR spectroscopy for real-time analysis of UV curing reactions has been compared to the widely used differentialphotocalorimetry(DSC) [66,67], IR radiometry [68] and laser-interferometry [62].

The distinct advantages of RTIR spectroscopy clearly appear from analysis of Table I.

Table I. Performance analysis of various methods of kinetic analysis.

TECHNIQUES	DSC [a]	IR-R [b]	LASER [c]	RTIR [d]	CURING
Response time (s)	>2	0.5	0.001	0.02	-
Light Intensity (mW/cm^2)	<4	<50	<1000	<500	500
Exposure time (s)	>10	>2	>0.01	>0.1	>0.1
Atmosphere	N_2	Air	Air	Air	Air
Sample temperature	<30°	<50°	<100°	<70°	<70°
Thickness control	poor	fair	fair	good	fair
Rate evaluation	yes	no	no	yes	-
Unsaturation content	poor	no	no	yes	-
Properties measurements	no	yes	no	yes	yes

a) DSC : Differential Photocalorimetry (DSC)
b) IR-R : Infra-red Radiometry
c) LASER : Laser-Interferometry
d) RTIR : Real-time Infra-red Spectroscopy

CHROMATOGRAPHY

Chromatography includes various experimental techniques designed to separate mixtures of compounds so that it is possible to understand the composition of complex mixtures. The principle of the chromatographic process involves the separation of a mixture into pure compounds by their differential adsorption properties when distributed between a two-phase system, one of which is stationary, the other being mobile. Each absorbent phase competes to adsorb the compounds being separated i.e., the stationary phase will retain the components which are the most easily adsorbed to varying extents, while the mobile phase carries them along with it, such that the mixture experiences two forces. It is feasible to separate a mixture if the ratio between the amount of a particular component in each phase differs from that of another component. Thus separation is established because of a partitioning of the sample components between the moving and stationary phases [69,70].

GAS CHROMATOGRAPHY

In gas-liquid chromatography, the stationary phase is a liquid held on a solid bead and the mobile phase is an inert gas. The sample is injected as a liquid and is then immediately volatilised. The components of the sample which are soluble

in the stationary phase distribute themselves between it and the mobile phase according to the principles of equilibria. By forcing an inert carrier gas through the chromatographic column, elution is possible. The rate at which a component elutes depends upon its tendency to dissolve in the stationary phase. Components which are highly soluble in the stationary phase will elute later than those which are only slightly soluble [69].

Qualitative analysis of the sample depends upon the time each component peak elutes, whereas quantitative analysis of the sample is dependent upon the area under each eluting peak. Theoretically the retention time data should enable identification of a particular component. The procedure however, is limited by the existence of several variables which will reduce the reproducibility of the retention times. An eluting peak may be identified by comparison with an authentic sample if its composition is suspected, followed by spiking the sample under investigation with the authentic sample. If no addiitional peaks elute and the area under the unknown peak increases, there is a good chance that the two are identical and the compound has been identified. Confirmation can be obtained by repeating the procedure using a different liquid phase.

GAS CHROMATOGRAPHY - MASS SPECTROMETER SYSTEMS

The effluent from a gas chromatograph is usually a small quantity ($10-^{12}$ to 10^{-3}g) of a pure compound or, less frequently, a simple mixture in the gas phase. This small amount of pure compound is ideal for direct transfer into a mass spectrometer source, providing the carrier gas (e.g. He) is largely removed first. The carrier gas is removed by separators which rely on either the faster diffusion of He, or preferential passage of the organic substrate through a membrane into the mass spectrometer. The spectrum of each component is obtained as it leaves the column. Identification of substances in very small quantities is possible (e.g., 10^{-9} to 10^{-12}g) by ionisation of the effluent vapour [42]. The molecular weight of each compound can be measured from the mass to charge ratio (m/z values) of the molecular ion formed. If no molecular ion is detected however, the structure of the compound, and hence the molecular weight can be deduced from the charged fragments (identified by their m/z values) produced by the breakdown of the molecular ion.

HARDNESS

The hardness of the film is related to the degree of cure and crosslink density [71]. Normally there is a good correlation

between pendulum hardness and residual unsaturation in the polymer film as determined by IR. The substrate will play an important part in determining hardness, particularly with thin films. A more exact evaluation of hardness can be made by measuring the damping by the coating of the oscillations of a pendulum (Persoz hardness [5], König pendulum hardness [5]. The König pendulum hardness tester is convenient to use and is particularly useful for small samples of cured coatings.[71]

The pendulum is enclosed in a case to eliminate draughts and to facilitate control of humidity. The release mechanisms which lower the pendulum onto the specimen and begin its oscillations are operated from outside the case. The apparatus may be standardised by adjusting the centre of gravity of the pendulum (by movement of a weight up or down a threaded rod) so that a time of 250 secs is obtained when the sample is plate glass. Thus the time taken for the amplitude of the oscillations to decrease from 6^{o} to 3^{o} from the vertical which is measured on a scale at the lower end of the pendulum.

The higher the degree of cure, the longer the pendulum will oscillate. The pendulum suspension points rock on a small area of the coating and so it is easy to avoid surface imperfections; at the same time it is desirable to take the mean of a number of measurements.

In taking the measurements it is important to realise that both the thickness of the coating and the hardness of the substrate have a marked influence on the results [3, 53]

GLOSS

The extremes of matt and high gloss [73, 74] are often wanted in photopolymerisable systems. High gloss is simpler to achieve than matt systems. Matt finishes may be obtained by introduction of a matting agent. However, the rheology of such systems as well as film properties must be monitored when incorporating matting agents. Gloss is obtained by careful consideration of several factors respectively, the nature of the matting agent and concentration. Acrylate systems tend to produce high gloss films and are difficult to modify with matting agents. The curing atmosphere, the curing of a system under aerobic or anaerobic conditions will also affect the gloss of a coating. It has been shown that gloss is markedly lower when curing is carried out in aerobic conditions. The lamp focus, intensity and distance from source also affect the gloss.

BULK POLYMERISATION

Bulk polymerisation traditionally has been defined as the formation of polymer from pure, undiluted monomers.

Incidental amounts of solvents and small amounts of catalysts, promoters and chain-transfer agents may also be present according to the classical definition.

The bulk polymerisation of acrylic monomers is characterised by a rapid acceleration in the rate. In the case of MMA (methyl metacrylate), an auto acceleration is observed between 20-40% conversion [75] and the formation of a crosslinked insoluble polymer network at low conversion [76], (which leads to a narrow molecular weight distribution).

The formation of a polymer network is thought to occur by a chain-transfer mechanism. The abstraction of a hydrogen atom from a neighbouring polymer chain, or oligomer, by the original radical (which dies in the process) generates a new radical at the site of abstraction. The subsequent growth of a branch or new chain radical at this point occurs as more monomers are added. Termination can occur by the combination of any two of these branched or chain radicals [77,78]

CALORIMETRIC METHODS

Photopolymerisation reactions which occur via chain reactions are generally exothermic since double bonds of monomers are converted into single bonds whenever the monomers add to polymer radicals. For this reason calorimetric studies of photopolymerisation have been carried out using a variety of calorimeter designs. Many examples of the application of calorimetry to UV curing have employed commercial differential scanning calorimeters (DSC) adapted to allow the sample to be irradiated with a UV lamp.

DIFFERENTIAL SCANNING CALORIMETRY

A differential scanning calorimetry (DSC) measures the rate of heat produced as well as the total amount of heat produced from a chemical reaction. In a polymerisation reaction this can easily be related to the rate of conversion of monomer to polymer and to the total amount of monomer polymerised.

The DSC has been used to study polymerisation in bulk, solution and emulsion systems. Both isothermal and temperature scanning modes have been employed.

USES AND ANALYSIS OF DATA

The basic data obtained from calorimetric analysis of a

photoinitiated polymerisation are in the form of an exotherm trace as shown in Fig.1.9. Here the rate of heat released by the sample (dH/dtin mcal/sec) is plotted versus the elapsed time of reaction.

Analysis of the isothermal polymerisation curves follows the procedure of Barrett [79]. The kinetic scheme used is that of a classical free radical polymerisation [80].

The total area A of the exotherm curve corresponds to the total heat of polymerisation of the sample.

$$\Delta H_{polym} = A \qquad (42)$$

The rate of polymerisation, R_p is given by

$$R_p = k\,[M] \qquad (43)$$

where [M] is the monomer concentration and k is the first order rate constant in sec^{-1}

$$-d[M]/dt = k[M] \qquad (44)$$

$$k = k_p\,(f\varepsilon[C]I_o/kt)^{1/2} \qquad (45)$$

For light initiated polymerisations with termination by interaction of two growing radicals, where:-

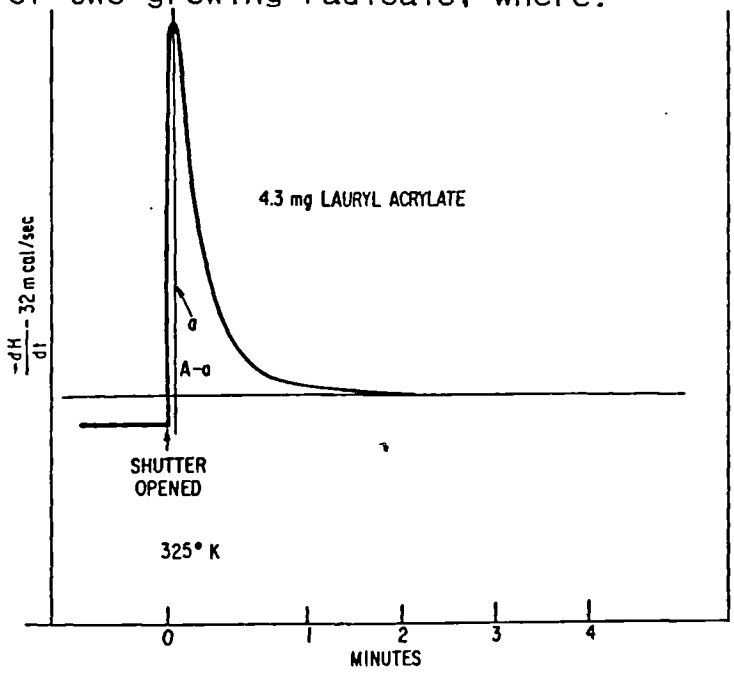


Fig. 1.9

k_p = propagation rate constant

k_t = termination rate constant

f = quantum yield for chain initiation

ε = initiator absorption coefficient

[C] = initiator concentration

I_o = incident light intensity

k is determined [79] from the experimental exotherm curve (Fig. 1.9) by applying at a given fractional conversion, a/A the relation,

$$k = (-dH/dt)/(A-a) \qquad (46)$$

where -dH/dt (mcal/sec) is the ordinate of the curve at the chosen fraction of conversion (a/A) and A-a (mcal) is the residual heat of polymerisation of the unreacted monomer.

The UV light intensity effect, and the initiator concentration may be varied to obtain the initiator concentration effect indicated equation (45).

FOURIER TRANSFORM INFRARED SPECTROSCOPY

FTIR spectroscopy is a classical example of the application of the uniqueness of Fourier's integral theorems, in which a complex wave function (interferogram) is transformed into an optical spectrum (signal versus frequency).

Fourier transform infrared spectrometers are based on the Michelson interferometer. A schematic diagram of the Michelson interferometer is shown in Fig. 1.10.

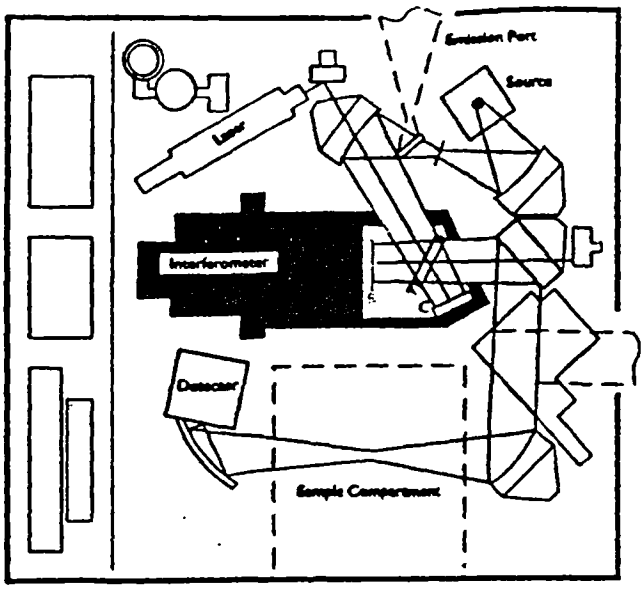


Fig. 1.10

A Michelson interferometer consists of three active components:

a) Beamsplitter b) A moving mirror c) A fixed mirror

The infrared signal is achieved as follows:

(i) Infrared light from the source impinges on the beamsplitter.

(ii) At the beamsplitter 50% of light is reflected to a moving mirror, 50% is transmitted to a fixed mirror.

(iii) The split beams are reflected from the fixed and moving mirrors to recombine at the beamsplitter. However, since the path length of the beam reflected from the moving mirror varies with respect to that from the fixed mirror on recombination an interference pattern is produced.

(iv) Using a continuum source an extensive interference pattern is produced, and when the Fourier Transform is applied, an infrared spectrum is obtained.

The added advantage of the FT-IR spectrometer is that it is frequency based, i.e. the infrared signal is referenced to a laser line emitted from a helium-neon laser and the spectral range does not have to be calibrated as with a dispersive system.

The other advantages of FTIR are:

Speed: Using a dispersive (monochromator) based infrared spectrometer, a spectrum is obtained by rotating a ruled grating to cover the range required in ten or more minutes. With a Michelson interferometer and Fourier Transformation, a complete spectrum is obtained during a single sweep of mirror B in Fig. 1.11.

Infrared Power at the Sample: At least 50% of the light from the source reaches the sample from a Michelson interferometer, unlike a dispersive system where a high proportion of source power is lost. This is particularly true at high resolution, where slits must be used and up to 95% of source light can be lost.

In a Michelson interferometer resolution is achieved by moving the mirror further. An iris or aperture is used to improve resolution, however, the loss of power from the source is not as great as occurs with a monochromator.

Signal to Noise Ratio: Because several spectra can be collected in a few seconds, the signal to noise ratio can be improved by the co-addition of a series of spectra collected from a number of scans.

Using an FT-IR spectrometer requires three essential stages:-

A. **Spectrometer Alignment:** If required, alignment involves optimisation of the beamsplitter angle to achieve maximum instrument response. The instrument response is displayed as an expanded interferogram (Fig 1.11).

   The beamsplitter is adjusted until the amplitude of the centre burst is at its maximum, but more importantly until the symmetry around the negative point is at its optimum.

B. **Collecting a Reference Spectrum:** A reference spectrum is collected as the first stage in producing an infrared spectrum from a sample. The reference of single beam spectrum (Fig. 1.11A)is a response curve of the FT-IR spectrometer.

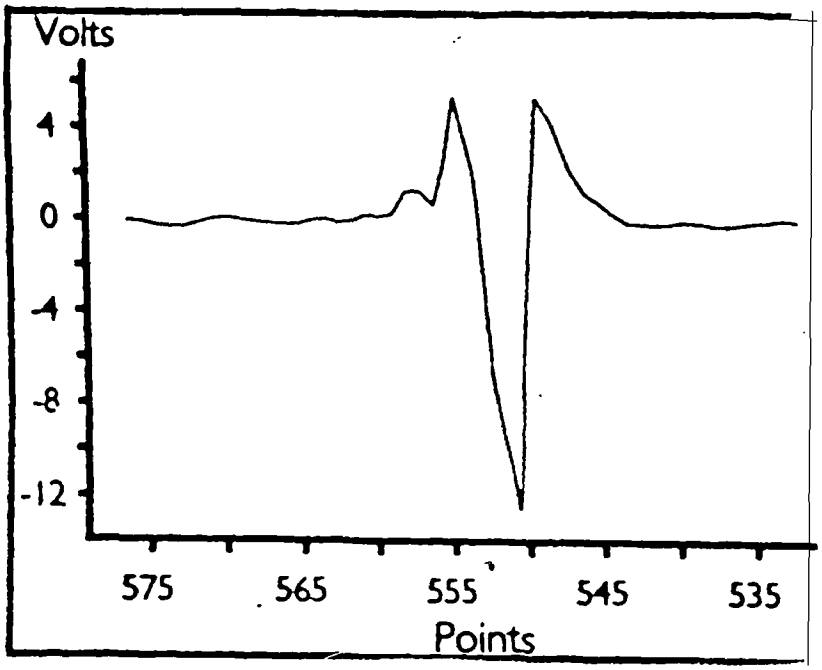
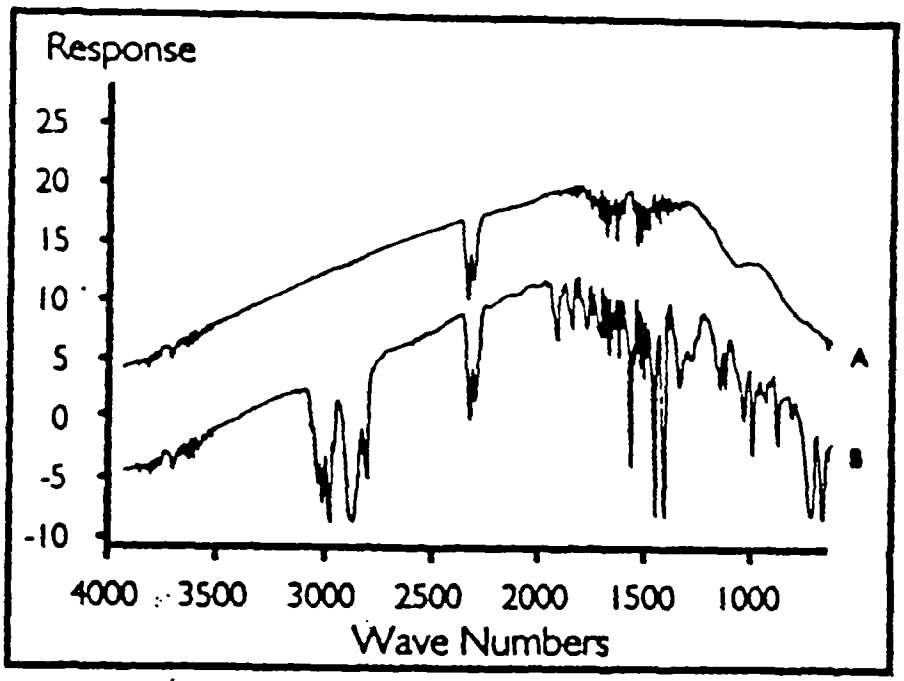


Fig 1.11



Response from an FT-IR Spectrometer
Top: no Sample Bottom: with Sample

Fig 1.11A

C. Collecting a Spectrum from Sample: The sample is placed in a sampling accessory and the spectrum is collected.

The ability to store and manipulate the data is a major advantage of computer interfacing, and at the present lower costs, is making FTIR spectroscopy available to many users.

ATTENUATED TOTAL REFLECTANCE SPECTROSCOPY

Attenuated total reflectance (ATR) analysis is a simple and sensitive technique which can be used to study the surface and interface of thin polymer coatings using crystals of varying refractive index.

Sample materials which are difficult to analyse by transmission measurements can often be characterised by ATR techniques. Unfortunately, certain limitations of the technique exist. High quality reproducible spectra will be achieved if the samples are of a flexible nature or on a flexible substrate, so as to effect a good contact between the sample and the crystal.

The ATR technique has been used successfully to analyse polymer films, fabrics, paper and rubber [81,82].

During analysis, infrared radiation is focussed onto the surface of the crystal at the entrance face at an angle of

incidence greater than the critical angle, where it will undergo total internal reflection. The critical angle is defined as follows:

$$\sin\theta_c = n_1/n_2 \qquad (47)$$

where n_1 is the refractive of the sample material and n_2 is the refractive index of the crystal. Under such conditions, incident radiation will be internally reflected at each crystal-sample interface (Fig. 1.12). The infrared beam however, will penetrate into the sample slightly. This penetration is known as an evanescent wave which will interact with sample molecules being either absorbed by the sample or reflected back to the crystal. After multiple internal reflections, the infrared radiation emerges from the crystal and is detected. The refractive index of the sample material varies in the region of an absorbance bond, thus the critical angle will also change giving rise to a distorted spectrum if it crosses over the angle of incidence. Increasing the angle of incidence will restore the total reflection condition eliminating the spectral distortion.

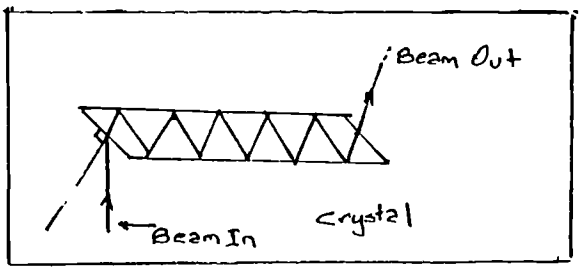


Fig. 1.12 An illustration of total internal reflectance for a parallelogram ATR crystal

The effect of the angle of incidence on the resulting spectra [83] and the systematic variation of the angle of incidence to enable depth profiling of multilayered samples has been reported [84,85].

Depth profiling can be achieved using different ATR crystals. Varying the crystals, each with a different refractive index, allows gradient trends within the film to be observed.

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CHAPTER 2

SYNTHESIS

Chapter 2. SYNTHESIS

2-(N-methyl-N-phenylamino-1-phenyl) ethanone

Method

4g of phenacyl bromide in 20 ml of dry toluene was placed in a round bottomed flask. A mixture of 2g (2.75 ml) triethylamine and 2.1g (2.132 ml) of N-methylaniline in 10 ml of toluene was added to the flask. The mixture was stirred under N_2 for 12 hours. After 12 hours, the yellow precipitate was formed and the solution was filtered. The toluene was removed from the filtrate using a rotary evaporator and yellow crystals were obtained. After recrystallisation from absolute ethanol clear yellow crystals formed.

Analysis, calculated for, $C_{15}N_{15}NO$, C, 79.97 ; H, 6.71 ; N, 6.21. Found C, 80.01 ; H, 6.77; N, 6.20.

Spectral Analysis, IR (cm^{-1}), 1734 (C-O of carbonyl stretch), 1600 (C_6H_5), 1377 (C-N stretch), 850 (C-N aromatic).

2-(N-methyl-N-phenylamino-1-phenyl) ethanol

Method

2g of 2-(N-methyl-N-phenylamino-1-phenylethanone was placed in 20 ml of dry methanol. While stirring the solution, 0.4g of $NaBH_4$ was carefully added to the solution. The reaction mixture was allowed to stand at room temperature with stirring for 20 minutes. The methanol was removed by rotary evaporator and the residue was diluted with 40 ml of water. The mixture was extracted with ether (2 x 20 ml). The ethereal extract was dried over $MgSO_4$. The ether solution was filtered and the ether removed by rotary evaporator. The aminoalcohol was obtained as red-brown oil. The product was distilled using high vacuum distillation.

Spectral Analysis: IR (cm^{-1}) 3061 (C_6H_5, C-H stretch) 2822 (CH_3, C-H stretch), 1589, 1571, 1501 (C_6H_5, C=C, ring stretch), 1370, (C-N stretch), 1121 (C-O) stretch.

Analysis calculated for $C_{15}H_{17}NO$: C, 79.35; H, 7.54; N, 6.16
Found: C, 79,96; H, 7.63; N, 6.20.

The following compounds were prepared in a similar way to that previously described.

1-Phenyl-1-(4-dimethylaminophenyl) methanol

1-Phenyl-1-[4-dimethylaminophenyl) methanone was used as starting material. The product was solid as white crystals.

Spectral Analysis: IR (cm^{-1}) 3353 (O-H stretch), 3042 (C-H stretch), 1577 (C_6H_5, C=C ring stretch), 1125 (O-H bend).

Analysis calculated for $C_{15}H_{17}ON$: C, 79.37 ; H, 7.54; N, 6.16
Found : C, 80.01; H, 7.93; N. 6.17.

2,2-Dimethyl-2-(N-morpholino)-1-phenyl ethanol

2,2-Dimethyl-2-(N-morpholino)-1-phenyl ethanone was used as starting material. The product was obtained as white powder after recrystallisation from hexane:ether.

Analysis: calculated for $C_{14}H_{21}NO_2$, C, 71.48; H, 8.93; N, 5.95; Found, C, 71.67; H, 9.02; N, 6.01:

Spectral Analysis : IR (cm^{-1}) 3355 (O-H stretch), 3041 (C-H stretch), 2845 (CH_3, C-H stretch), 1600 (C_6H_5, C=C stretch), 850 C-N aromatic stretch.

2,2-Dimethyl-1-(4-dimethylaminophenyl)-2-morpholino ethanol

2,2-Dimethyl-1-(4-dimethylaminophenyl)-2-morpholino ethanone was used as starting material. The product was obtained as a white powder after recrystallisation from hexane:ether.

Analysis: calculated for $C_{16}H_{26}N_2O_2$, C, 69.08; H, 9.35; N, 10.07, Found, C.70.07; H, 9.78; N, 10.05.

Spectral Analysis: IR (cm^{-1}, 3363, (O-H), 3033 (C_6H_5, C-H), 2831 (CH_3, C-H), 1597, 1500 (C_6H_5, C=C), 1365 (C-N), 1120 (C-O), 8.49 (C-N, aromatic).

2-Methoxy-2-phenyl-1,1-diphenyl ethanol (1)

All glassware was dried in an oven at 140°C and flushed with dry nitrogen during cooling. 10 ml of 1.0M ketone-(2-methoxy-2-phenyl-1-phenyl ethanone) in dry toluene was placed in a three-necked flask and started to pass nitrogen. 10 ml of 1.8M PhLi in cyclohexane was added in dropwise at -78 C. (Dry ice + acetone).

After the addition of the above compounds, the reaction was allowed to warm to room temperature and stirred for one hour. After hydrolysis with "Rochelle Salt", the organic layer was

dried over $MgSO_4$. The mass spectrum of the residue showed that the product was a mixture of starting material (Fig. 1).

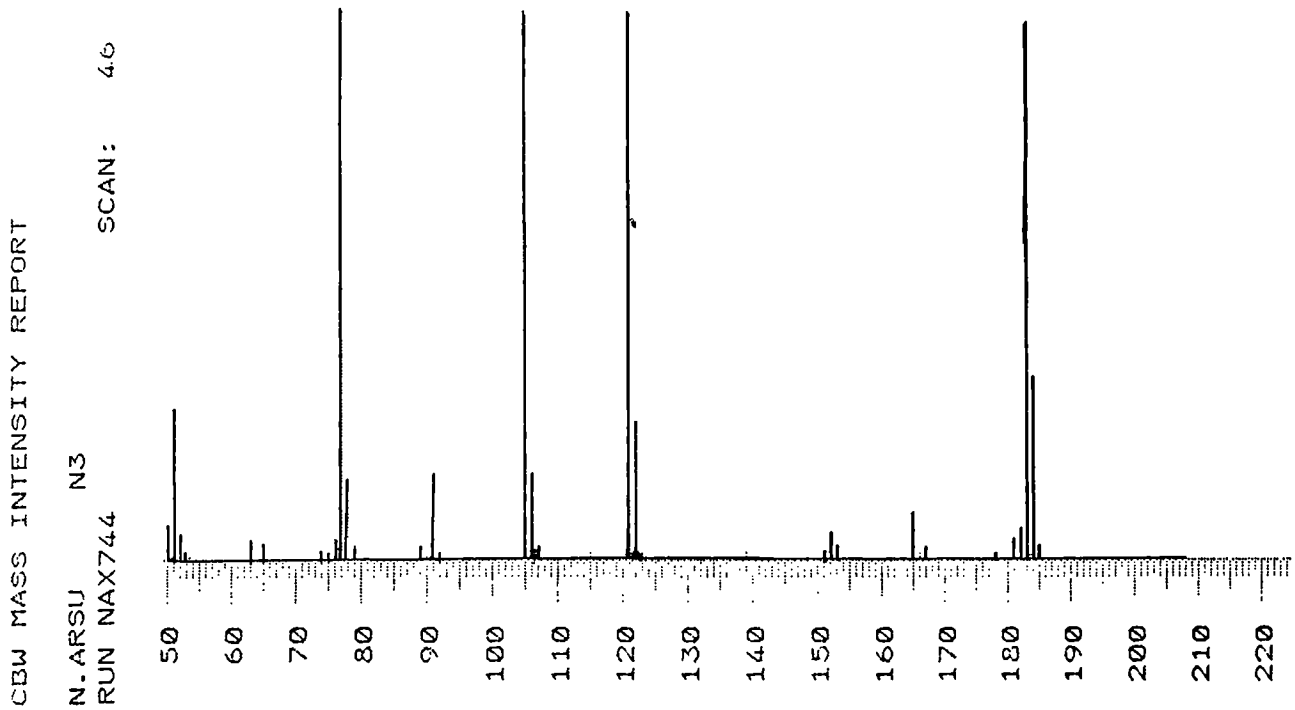
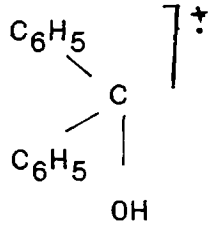
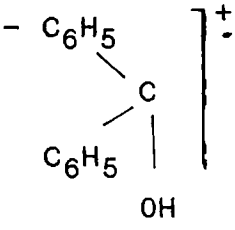
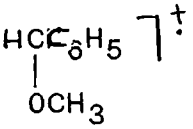
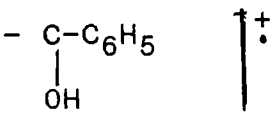


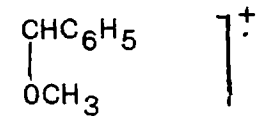
Fig. 1 The Mass Spectrum of 2-Methoxy-2-Phenyl -1, 1-Diphenyl Ethanol

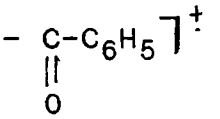
183 - 

184 - 

121 - 

106 - 

122 - 

105 - 

77 - $C_6H_5^+$

N-Isopropylmorpholine [2]

First method

A mixture of 10 ml (0.125 mol) of morpholine and 22 ml (0.25 mole) of isopropylbromide was heated under reflux in an oil bath for 12 hours. After removal of morpholinohydrobromide by filtration, fractionation of the filtrate gave isopropylmorpholine. The mass spectrum of isopropylmorpholine is given in Fig. 2, yield: 22%. The boiling point was bp: 156°C $bp_{lit[3]}$ 153-157°C.

Analysis, calculated for $C_7H_{15}ON$, C, 65.07; H, 11.70; N, 10.88 Found, C, 64.96; H, 12.01; N, 10.94.

^1H NMR (100MHz) : 1.05 (d,3H), 1.7 (d,3H), 2.65 (q,4H), 3.8 *(m,4H), 4.3 (m,1H).*

The following compounds, isopropylpiperidine and isopropylpyrrolidine were prepared in a similar way as previously described.

Isopropylpiperidine [2]

Piperidine was used as a starting material. The product was a yellow liquid and distilled by using high vacuum distillation.

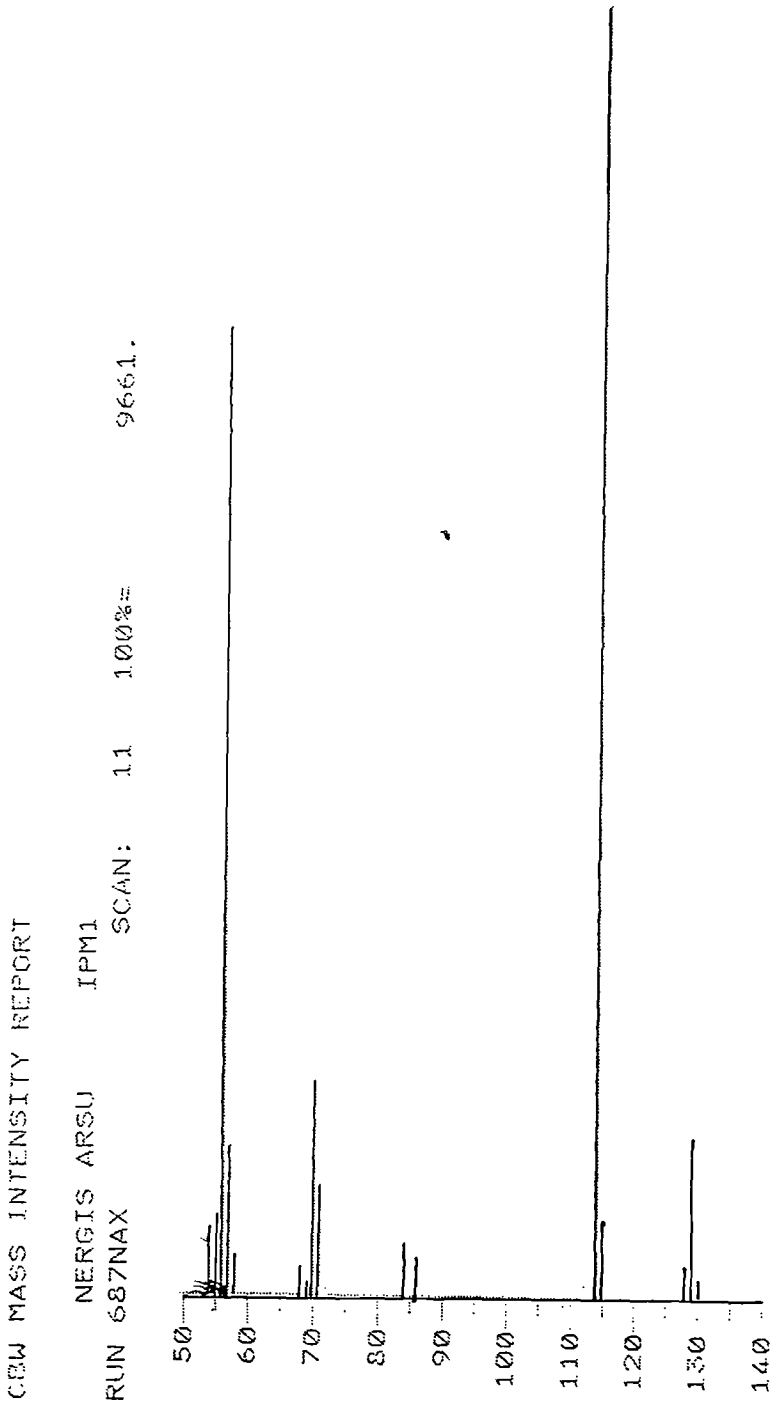
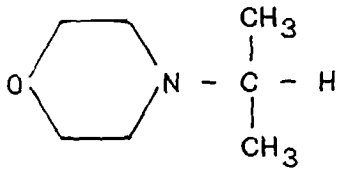
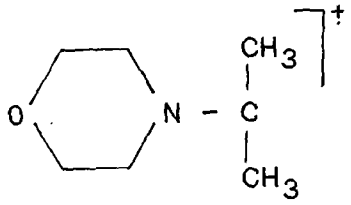
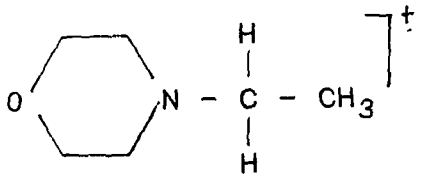
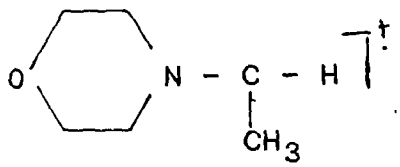


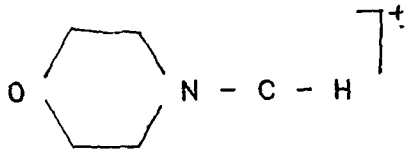
Fig 2.2 The Mass Spectrum of N- Isopropylmorpholine

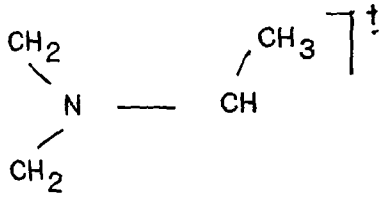
129 

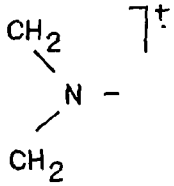
128 

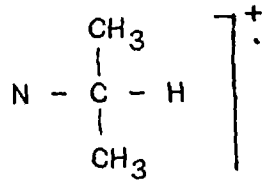
115 

114 



70 

51 

57 

Analysis, calculated for $C_8H_{17}N$; C,75.60; H, 13.38; N, 11.02; Found, C, 76.00; H, 13.56; N, 11.08.

^1H NMR (100MHz) : 1.05 (q,6H), 1.45 (m,4H), 2.65 (m,4H), 4.25 (m,1H).

Isopropylpyrrolidine [2]

Pyrrolidine was used as a starting material. The product was a dark brown liquid, after distillation by using high vacuum distillation a yellow liquid was obtained.

Analysis, calculated for $C_7H_{15}N$: C,74.34; H, 13.27; N, 12.38 Found, C, 74.96; H, 13.73; N, 12.52.

^1H NMR (100MHz) : 1.05 (t,3H), 1.15 (t,3H), 1.75 (m,4H), 2.65 (m,4H), 3.85 (M,1H).

1-Methyl morpholino acetonitrile [4]

2.8 ml of acetaldehyde and 9.5g of sodium-bisulphate solution in water were placed in a flask and 4.3 ml of morpholine was added. After addition of 3.25g of potassium cyanide; the reaction mixture was refluxed for 2 hours. The product was extracted with ether, and dried over $MgSO_4$. The product was obtained as a colourless liquid.

^1H NMR (100MHz) : 1.4 (d,3H), 2.6 (m,4H), 3.8 (m.4H), 4.1 (m,1H).

N-Isopropylmorpholine [4]

Second method - Grignard Reaction

3g of dry magnesium turnings were placed in a 100 ml three-necked flask, fitted with a dropping funnel, a mechanical stirrer and a reflux condenser. 2.0 ml of dry bromomethane in 7.0 ml of sodium dried ether was slowly added to the flask. After a whole bromomethane run, the solution was warmed gently on a water bath to promote the start of the reaction. The solution became cloudy after some considerable heating, and finally turned to a cloudy grey in appearance and this was accompanied by gentle effervescence. The latter was an indication that the reaction had begun. The heat was then removed and the exothermic reaction was allowed to drive the reaction. The remaining 5 ml of bromomethane in 20 ml of dried ether was added dropwise at a rate so as to maintain refluxing and to maintain a gentle reaction. Following the addition of all the starting material (1.5-2 hours) the mixture was refluxed by stirring over a hot bath at approximately 40^oC for 2 hours, when all the magnesium had disappeared.

When all the magnesium had disappeared, methylmorpholino-acetonitrile diluted in dry ether, was slowly added to maintain the reaction mixture in a state of reflux, i.e., the rate of addition of the methylmorpholinoacetonitrile - ether solution was equal to the rate of reflux. When all the methylmorpholinoacetonitrile was added, the reaction mixture was warmed and refluxed for 2 hours, and then left to cool slowly overnight. The mixture was then filtered. The excess ether was removed carefully on a rotary evaporator to give the final product.

1,3 - Dimorpholinopropane

1,3-Dibromopropane (50g, 0.247 moles) was added dropwise with stirring to a solution of morpholine (70g, 0.8 moles) in toluene (60 cm^3). After one hour, (during which time a white crystalline mass had formed), water (20 cm^3) was added and this was saturated with sodium hydroxide. The toluene layer was decanted off and the aqueous layer extracted further with toluene (3 x 50 cm^3). The extracts were combined, dried ($MgSO_4$), and the solvent removed on a rotary evaporator to give a pale yellow oil. This was distilled under reduced pressure to give a colourless oil.

B.p. 124-127^{o}C at 1.5 mm Hg.

^{1}H (NMR) : 3.6 (8H, m) ; 2.2 (12H, m), 1.6 (2H, m)

Analysis, calculated for $C_{11}H_{22}N_2O_2$, C, 61.64; H, 10.35; N, 13.07; Found, C.61.88; H,10.51; N, 13.01.

Arylation of Acrylates [5]

2.1 ml (20 mmol) of benzylbromide and 4 ml (40 mmol) methylacrylate in 5 ml toluene were placed in a three-necked round bottomed flask and 25 mmol (6 ml) tri-n-butylamine was added to this mixture followed by 0.3 mmol (0.066g) of palladium acetate. 0.8 mmol (0.208g) triphenylphosphine was added to the flask and the mixture was heated under reflux under argon for 12 hours.

The reaction mixture was cooled and a few ml of dilute HCl was added. After filtration, it was dried over $MgSO_4$ and the solvent evaporated by using a rotary evaporator.

The following acrylates were partially arylated except methyl-methacrylate.

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate

^{1}H NMR (100MHz) : 7.65 (m,5H), 2.98 (t,2H), 6.40 (m, 4H), 4.3 (q.4H), 2.2 (s,2H), 1.55 (m,2H), 0.9 (d,3H).

1,6-Hexanedioldiacrylate (Partially arylated)

7.5 (m,5H), 6.3 (m,3H), 4.15 (q,2H), 2.95 (t,2H), 1.7 (m,1H), 0.9 (d,).

Methylcinnamate

Methylmethacrylate was used as a starting material.

^{1}H (NMR) : 7.3 (m,5H), 3.8 (s,1H), 2.3 (s,1H), 1.25 (s,3H).

Pentaerythritoltriacrylate (Partially acrylated)

^{1}H NMR : 7.5 (m,5), 6.3 (m,3H), 4.2 (m,3H), 2.8 (m,1H), 2.3 (m,1H), 0.9 (m,3H).

2-Methyl-1-[4-(methylthio)phenyl-2-morpholino]propane-1-ol [6]

Method

1g of $LiAlH_4$ was weighed carefully into a dry flask and 30 ml of Na dried ether was added to the flask and the mixture was stirred at room temperature. 1g of Irgacure 907 was dissolved in 10 ml of dried ether. The solution was placed in a dropping funnel and added slowly and carefully into the flask. After adding the solution the reaction mixture was allowed to stand at room temperature for 10 mins. The reaction mixture was then refluxed for 4 hours. The solution was filtered and dried over $MgSO_4$. After evaporation of ether, the crude product was obtained in a form of white powder. The product was obtained after recrystallisation from hexane-ether mixture. Mp : 143^oC

Irg-907: 2-Methyl-1-[4-(methylthio)phenyl-2-morpholino] propane-1-one

Analysis, calculated for $C_{15}H_{23}nO_2S$, C, 64.02; H, 8.24; N, 4.98; Found, C, 64.06; H, 8.26; N.4.79

IR (cm^{-1}) : 3323 (O-H), 29.74, 2851 (C-H), 1536, 1485 (C_6H_5, C=C ring stretch, 1444 (C-N ring stretch).

2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-ol [6]

2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl-butan-1-one was used as a starting material. Mp: 106°C

Analysis, calculated for $C_{23}H_{26}N_2O_2$. C,78.96; H,8.75; N,7.60; Found C,77.93; H,8.98; N,7.53.

IR (cm^{-1}) 3378 (O-H stretch), 2855 (CH_3, C-H stretch), 1570, 1517 (phenyl) C=C ring stretch, 1128 (O-H bent) 852 (C-N, aromatic)

Erythro-2-morpholino-1,2-diphenyl ethanol [7]

1g (5 mol) of transstilbene oxide and (2.5 ml) 1 molar equivalent of distilled morpholine was refluxed for 12 hours with vigorous stirring. The reaction was followed by silica gel TLC analysis. The product was extracted with diethylether and excess of morpholine was separated by addition of 5 ml of distilled water. The combined organic layers were washed with distilled water several times to completely remove residual morpholine. The solution was dried over anhydrous magnesium sulphate, the solvent was removed on a rotary evaporator. The crude product was recrystallised five times from absolute ethanol. Yield 67%. Mp = 121°C. $Mp_{(lit)\ [7]}$ = 122°C.

Analysis, calculated for $C_{18}H_{21}NO_2$, C, 76.30; H, 7.54; N, 5.01; Found, C, 76.43; H, 7.56; N.4.93.

^1H NMR (100MHz) : 2.50 (m,2H), 2.70 (m,2H), 3.3 (s,1H), 3.8 (m,4H), 5.3 (d,1H), 7.0 (m,4H), 7.4 (m,6H).

This method was used to prepare erythro-2-piperidinyl-1,2-diphenylethanol and erythro-2-pyrrolidinyl-1,2-diphenylethanol Piperidine and pyrrolidine respectively were used instead of morpholine for these two preparations.

Erythro-2-piperidinyl-1,2-diphenylethanol [7]

The product was obtained as cream crystals. After recrystallisation from absolute alcohol, white crystals were obtained.
Mp: 100°C

Analysis, calculated for $C_{20}H_{22}NO$, C, 82.15; H, 7.58; N, 4.79; Found, C, 81.98; H, 7.96; N, 4.99.

Erythro-2-pyrrolidinyl-1,2-diphenyl ethanol [7]

Pyrrolidine was used as one of the starting materials. The product was obtained as dark brown crystals. After recrystallisation from absolute ethanol, white crystals were obtained.
Mp = 89°C $Mp_{lit\ [7]}$ = 92°C

S-(-)-N-Methyl-1,1-diphenylprolinol [8,9]

A solution of S-(-1-,1-diphenylprolinol (1g) (4mmol) in 5.8 ml of water was added slowly dropwise to a stirred solution of 88% HCO_2H (8g) and 37% aq HCHO (6.2g) under nitrogen at 5^oC.

Following the addition of the solution, the reaction mixture was allowed to warm up to room temperature with continuous stirring. The solution was then heated under reflux for 12 hours. The reaction mixture was cooled and basified with 50% aq NaOH. The product was extracted with ether and dried over Na_2SO_4. The mixture was filtered the following morning and the excess of ether was removed by using a rotary evaporator. The product was obtained as white crystals and recrystallised from absolute ethanol.

Analysis, calculated for $C_{18}H_{21}NO$, C, 80.86; H, 7.92; N, 5.24; Found, C,81.00; H, 8.04; N, 5.14.

^1H NMR : 7.6-7.2 (m, 8H), 3.05 (m,1H), 2.95 (m,1H), 1.7 (m,3H), 1.6 (m,2H).

R-(+)-N-Methyl-1,1-diphenylprolinol [8,9]

This compound was prepared according to the method which was given for the preparation of S-(-)-N-methyl-1,1-diphenylprolinol. The product was obtained as white-pink crystals and white crystals were obtained after recrystallisation from absolute ethanol.

Analysis : calculated for $C_{18}H_{21}NO$, C, 80.86; H, 7.92; N, 5.24; Found, C, 80.83; H, 7.61; N, 5.53.

Phenanthraquinoxaline [6,10]

4.1g of phenanthraquinone was dissolved in glacial acetic acid, and then 2.1g of O-phenylenediamine in glacial acetic acid solution was added to this mixture and heated for 15 mins on a water bath. The reaction mixture was cooled and diluted with water, filtered and the product recrystallised from dilute alcohol. Mp: 215^{o}C $Mp_{lit[6]}$: 217^{o}C

Analysis, calculated for $C_{20}H_{12}N_2$, C, 85.7; H, 4.28; N, 10.1; Found, C, 86.1; H, 4.4; N, 10.2.

Acenaphthoquinoxaline [6,10]

The method used to prepare phenanthroquinoxqline was also used to prepare acenaphthoquinoxaline. 3.6g of acenaphthoquinone was used as a starting material.

Analysis, calculated for, $C_{18}H_{10}N_2$, C, 85.0; H,3.94; N, 5.51; Found, C, 86.01; H,4.01; N,5.83.

EXPERIMENTAL

INSTRUMENTATION

The ^{1}H NMR spectra were recorded on a Jeol PMX-100 spectrometer using tetramethylsilane as an internal standard.

The mass spectra were recorded on a Kratos MS30 Electron Impact Instrument linked to a Kratos DS50 Data System.

Melting points were determined on a melting point microscope (Zeiss, equipped with a Mettler FP Hot Stage and FB80 processor) and are corrected.

Elemental Analysis was carried out using a Carlo Erba Strumentazione Elemental Analyzer Model 1106.

Infrared spectra were recorded on a Perkin Elmer Infrared Spectrometer.

Materials

Trimethylolpropanetriacrylate (TMPTA) was obtained from (Aldrich), 1,6-hexanedioldiacrylate (Aldrich), pentaerythritol-triacrylate (Aldrich), methylacrylate (Aldrich), were all used as received.

Solvents for Synthesis

Benzene, toluene, diethyl ether were obtained from (BDH Chemicals Ltd.) and were dried by the addition of sodium wire, 24 hours before use.

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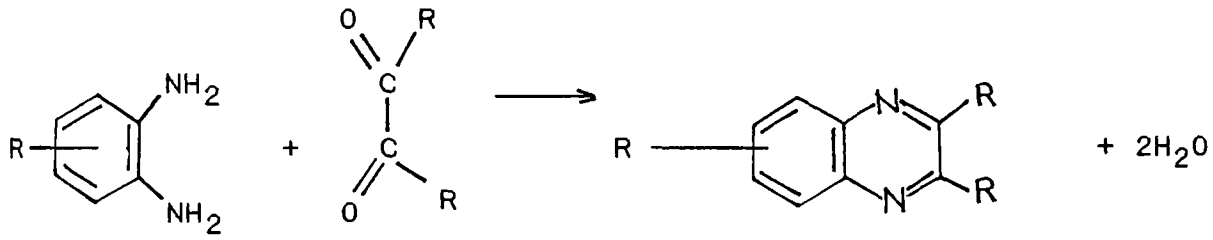
CHAPTER 3

QUINOXALINES AS PHOTOINITIATORS

Chapter 3. QUINOXALINES AS PHOTOINITIATORS

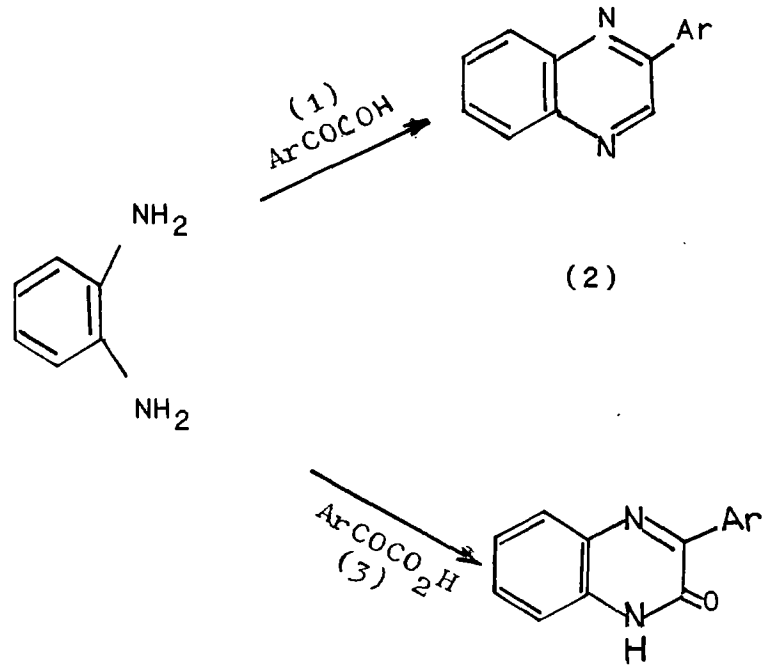
A. Preparation of Quinoxalines from O-Diamines

The classical synthesis of quinoxalines involves the condensation of an aromatic O-diamine and α-dicarbonyl compound as shown in Scheme 3.1



Scheme 3.1

Substituted phenylglyoxals (1) are the starting α-dicarbonyl compounds for the synthesis of 2-arylquinoxalines (2) [1], and the corresponding aryl α-ketoacids (3) yield 3-aryl-2-quinoxalines (4) [1,2].



(2)

(4)

Scheme 3.2

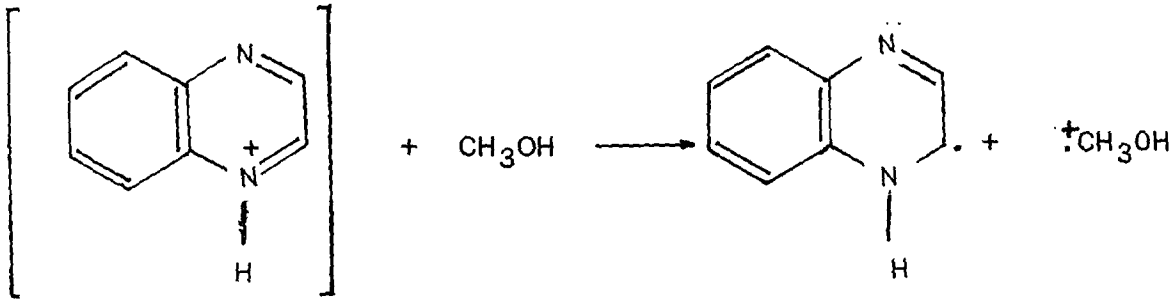
Photochemical Reactions

It has been reported [3] that substitution of quinoxaline takes place at C-2 when it is irradiated in ether, methanol and ethanol. The intermediate in the reaction is the quinoxaline radical (5).

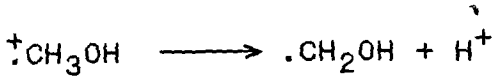
The UV irradiation of quinoxaline in methanol yields radicals, not by hydrogen abstraction, but by protonation of the first singlet excited state, followed by exciplex formation [4].

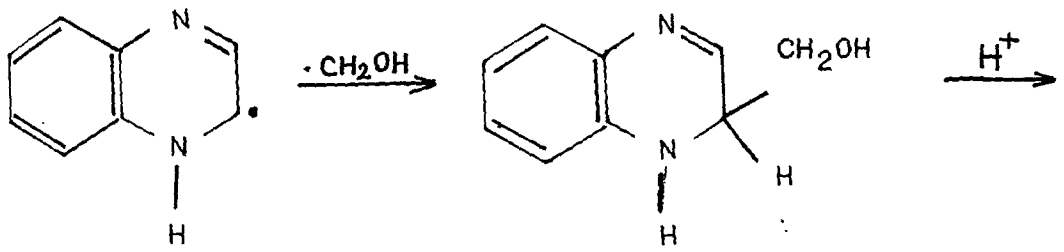
Irradiation of quinoxaline in acidified methanol furnishes 2-methylquinoxaline, and the reaction is suggested to go through a pathway involving electron transfer from the solvent to an excited state of the protonated quinoxaline (Scheme 3.3) [5].

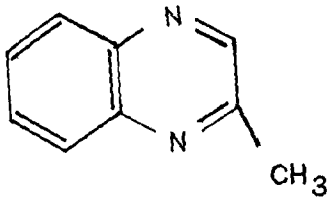
The photoinduced polymerisation of methyl methacrylate in the presence of 2,3-diphenylquinoxaline and 6-acrylamido 2,3-diphenylquinoxaline polymers has been investigated (6).



(5)







Scheme 3.3

$$C \xrightarrow{h\nu} C^*$$

$$C^* + R_DH + M \longrightarrow CH^{\cdot} + R_D^{\cdot}$$

$$CH^{\cdot} + M \longrightarrow MH^{\cdot} + C$$

Where C = Quinoxaline

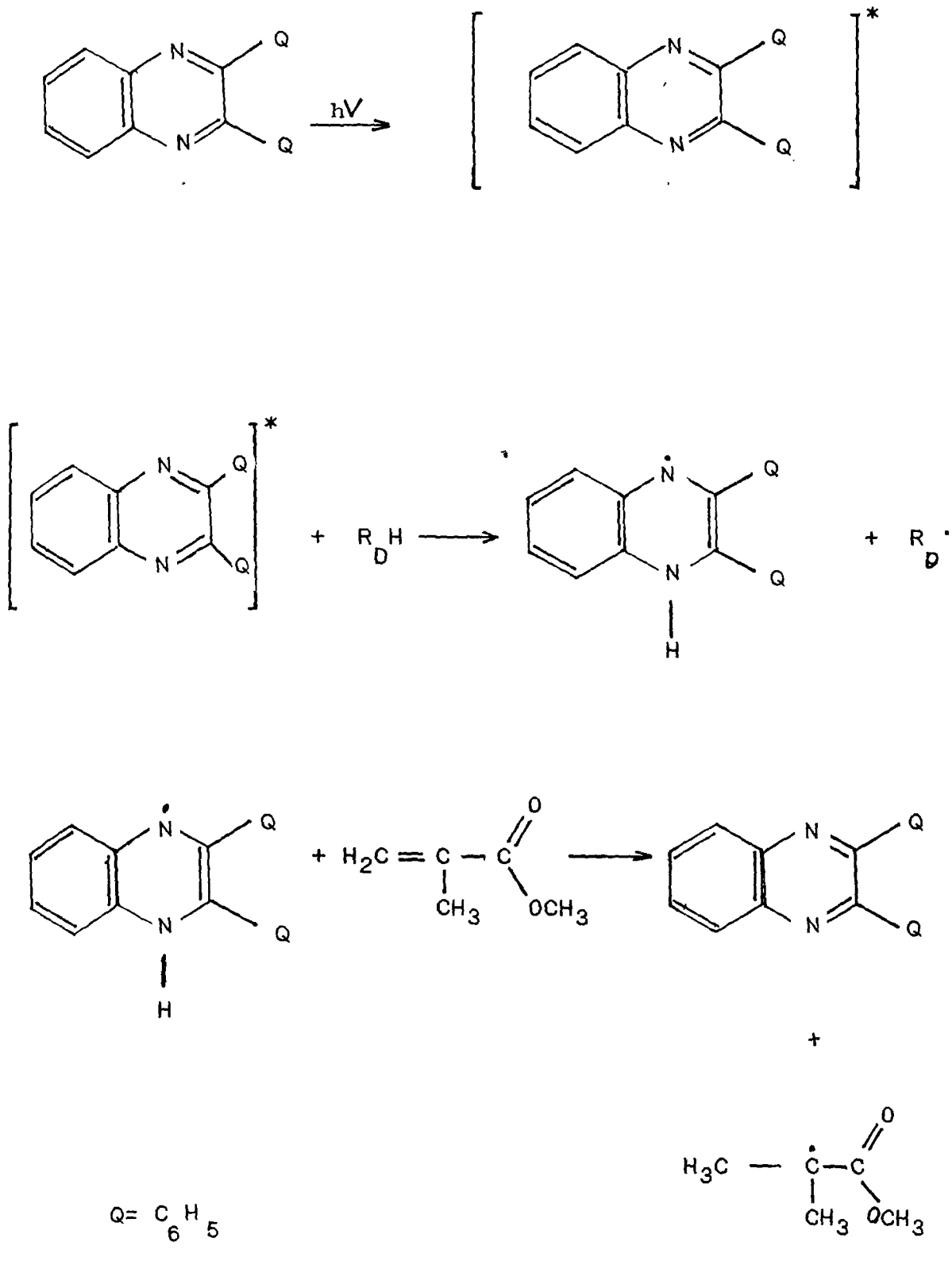
M = Monomer

R_DH = H-donor

As photoexcited quinoxaline molecules are capable of hydrogen abstraction, which can be followed by electron transfer, the formation of starting radicals in the considered system has been referred to a hydrogen transfer from a H-donor to monomer molecules with monohydroquinoxaline radicals as transferring reagent (Scheme 3.4) [6].

UV irradiation of carbonyl and heterocyclic (2,3-diphenylquinoxaline and acenaphthoquinoxaline) in the presence of aminoalcohols leads to fragmentation of the alcohols into benzaldehyde and N-arylamines [7]. These reactions will be discussed with more detail in Chapter 7.

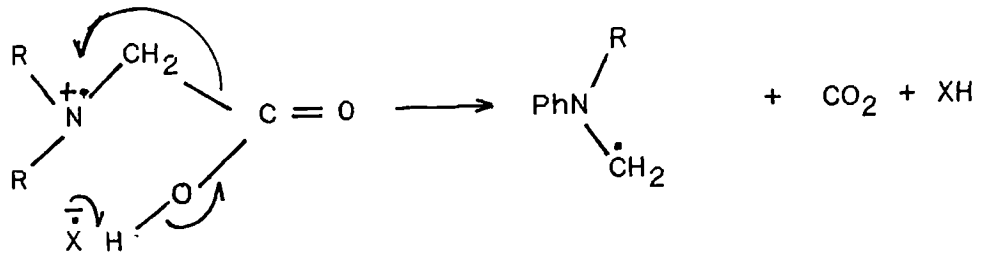
Chemical reaction usually occurs via intermediates such as exciplexes and radical ions, undergoing a proton transfer reaction.



Scheme. 3 . 4

Several heterocyclic compounds have been found to be efficient 'sensitisers' for the decarboxylation of carboxylic acids. Alkanoic acids give alkyl radicals and carbon dioxide on irradiation in the presence of acridine [8], quinoline [9,10] and riboflavin [11]. The bases trap the alkyl radicals formed in the reaction. These reactions can also occur intramolecularly [7]. All these reactions probably occur by an initial protonation of the basic singlet excited state of the heterocyclic compound.

Derivatives of tertiary amines which fragment in an electron transfer process have the potential to drive an electron transfer in the right direction by overcoming the back electron transfer process. N-arylglycines and many related acids have been found to fragment on undergoing electron transfer reaction with ketones (including quinones) [9,12] heterocyclic compounds and dyes [13], aromatic hydrocarbons [14] and nitroaromatics [15].



R=H or CH_3

The driving force for this reaction is provided by the elimination of the stable molecule of carbon dioxide. A combination of N-acrylglycines with dyes and other sensitisers [17] including the hexaarylbisimidazoles [18] have been used. The zwitterionic character of the aminoacids does, unfortunately, tend to render them rather insoluble in typical curing formulations.

It is well established that the combination of many dyes with a tertiary amine provides an excellent Type II photoinitiator system for the polymerisation of acrylates and related compounds [19-21]. Clearly, of particular importance, is the possibility that this combination can be used with visible light. Since many dyes are photobleached by amines these systems come into the class of photobleachable initiators which are valuable for curing thick films. The bleaching arises from reduction of an excited state of the dye (usually the triplet state) by the amine [22].

$$Dye_{T_1} + (RCH_2)_3N \longrightarrow [D\dot{y}\dot{e}(RCH_2)_3\overset{+}{\dot{N}}]$$

Exciplex or solvent separated ion pairs

$$\downarrow$$

$$D\dot{y}eH + (RCH_2)_2NC\cdot HR$$

Semi reduced dye

The reduced dye may undergo further reduction giving the leuco dye or disproportionate giving leuco dye and regenerated dye.

Reduction

$$D\dot{y}eH + (RCH_2)_2\,N\dot{C}HR \longrightarrow Dye\,H_2 + \text{Enamine}$$

leuco dye

Disproportionation

$$2\,D\dot{y}e\,H \longrightarrow Dye\,H_2 + Dye$$

In the course of irradiating thick films the initiating process depletes the amount of dye progressively from the irradiated surface downwards. This bleaching process is of course in competition with regeneration of the dye by the

action of oxygen upon the semi reduced and leuco dye.

$$Dye^{\bullet}H + O_2 \longrightarrow Dye + HO_2^{\bullet}$$

$$Dye\ H_2 + O_2 \longrightarrow Dye + H_2O_2$$

Consequently, for efficient bleaching, high light intensities are required so that the process competes effectively with migration of oxygen from the atmosphere into the film. If photobleaching is efficient, the cured film will initially appear to be colourless but as oxygen diffuses into the film the colour will be restored.

The efficiency of regeneration is very dependent upon the types of amine used.

Quinoxalines are similar to dyes in that the photochemical reaction produces a reduced species which may regenerate the starting material following reaction with oxygen or possibly via a disproportionation reaction.

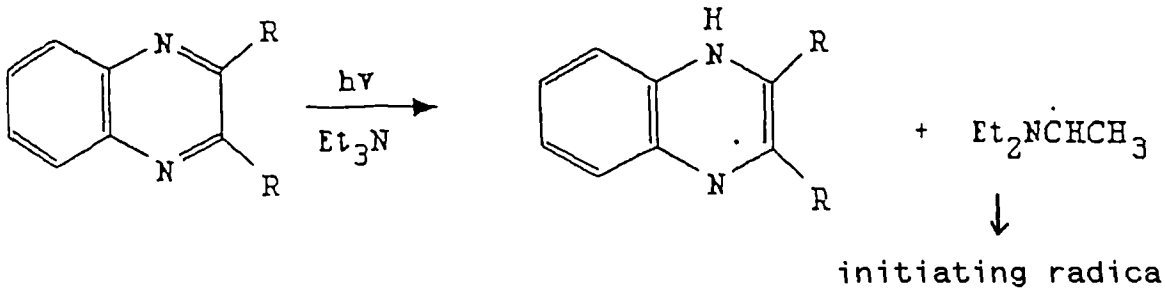
RESULTS AND DISCUSSION

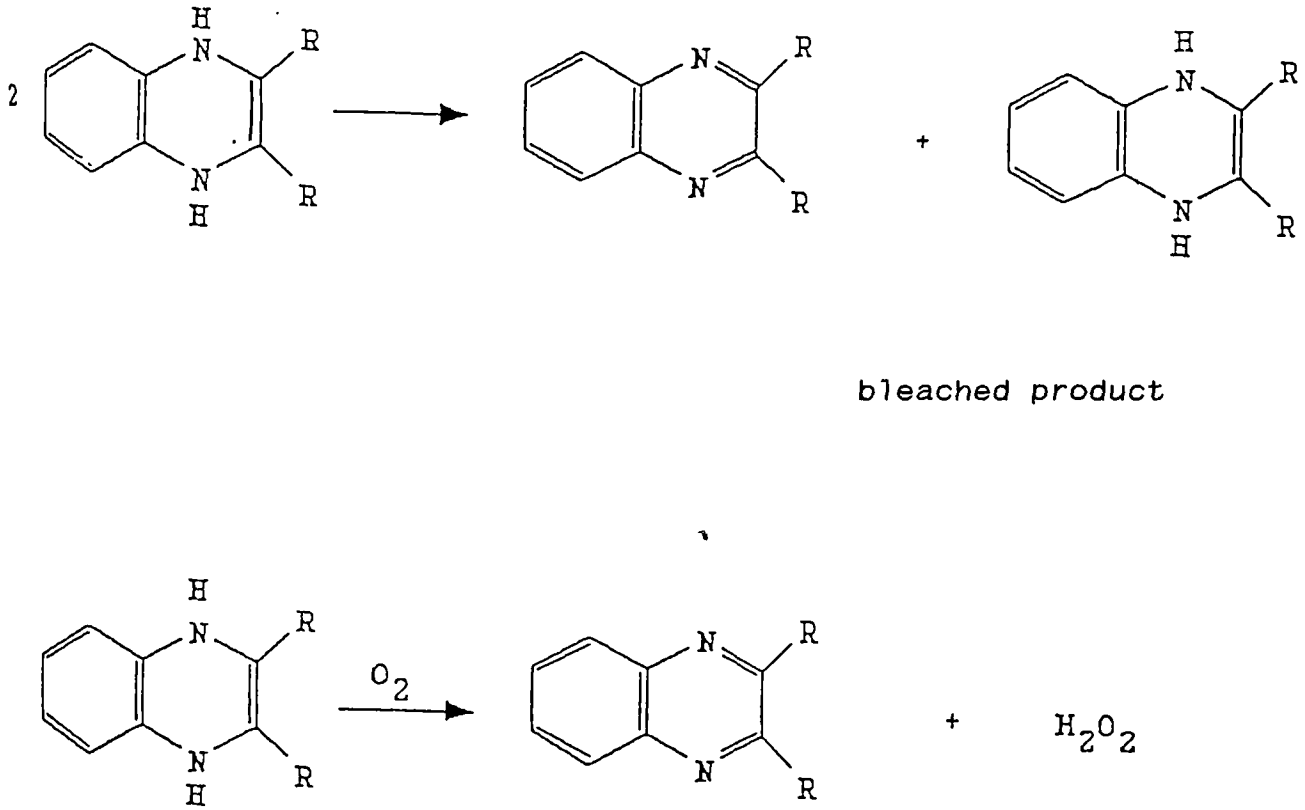
Quinoxalines as Photoinitiators

The quinoxaline nucleus is to be found in a number of dyes and closely related structures are e.g. in riboflavin. Many of these materials show poor light fastness due to their ability to form excited states which abstract hydrogen from suitable C-H bonds. Quinoxalines like quinolines will induce free radical polymerisation via hydrogen abstraction from alkanes [6].

These materials can be classed as photobleachable and recyclable photoinitiators. Some earlier work by R.S. Davidson established that quinoxalines are photoreduced by tertiary amines and that their reduction products are re-oxidised by oxygen to give the starting material.

A simplified mechanism which explains such phenomena is shown in Scheme 3.5.





Scheme.3.5.

If oxygen is present in solution during irradiation it is possible that it will react with the semi reduced quinoxaline. It will be noted that hydrogen abstraction possibly via electron transfer followed by proton transfer from the tertiary amine leads to an α-aminoalkyl radical, such radicals are known to be good initiators for acrylate polymerisation [23].

The photoinduced polymerisation of 2-ethyl-2-(hydroxymethyl-1,3-propanediol triacrylate in the presence of 2,3-diphenylquinoxaline, 2,3-dimethylquinoxaline, quinoxaline, styrylquinoxaline, acenaphtho [1,2-b] quinoxaline, phenanthro [9,10-b] quinoxaline and dichloroquinoxaline with or without N-methyldiethanolamine were investigated.

Two different methods were used to examine the efficiency of various quinoxalines and the results are shown in Fig. 3.1 and Fig. 3.2. The two methods used were UV curing of thin films and bulk polymerisation. The samples which contained different amine concentrations and different initiator concentrations were tested in air atmosphere.

As can be seen from Fig. 3.1 and Fig. 3.2, the quinoxalines when used with a good amine synergist such as N-methyldiethanolamine are efficient Type II initiators.

Q1 = 0.1% Quinoxaline/3% NMDEA/TMPTA

Q2 = 0.1% Dimethylquinoxaline/3% NMDEA/TMPTA

Q3 = 0.1% 2,3-Diphenylquinoxaline/3% NMDEA/TMPTA

Q4 = 0.1% Phenanthro [9-10-b] quinoxaline/3% NMDEA/TMPTA

Q5 = 0.1% Acenaphtho [1,2-b] quinoxaline/3% NMDEA/TMPTA

Q6 = 0.1% Dichloroquinoxaline/3% NMDEA/TMPTA

P1 = 1% Quinoxaline/10% NMDEA/TMPTA

P2 = 1% Dimethylquinoxaline/10% NMDEA/TMPTA

P3 = 1% 2,3-Diphenylquinoxaline/10% NMDEA/TMPTA

P4 = 1% Phenanthro [9-10-b] quinoxaline/10% NMDEA/TMPTA

P5 = 1% Acenaphtho [1,2-b] quinoxaline/10% NMDEA/TMPTA

P6 = 1% Dichloroquinoxaline/10% NMDEA/TMPTA

S1 = 2% Quinoxaline/10% NMDEA/TMPTA

S2 = 2% Dimethylquinoxaline/10% NMDEA/TMPTA

S3 = 2% 2,3-Diphenylquinoxaline/10% NMDEA/TMPTA

S4 = 2% Phenanthro [9,10-b] quinoxaline/10% NMDEA/TMPTA

S5 = 2% Acenaphtho [1,2-b] quinoxaline/10% NMDEA/TMPTA

S6 = 2% Dichloroquinoxaline/10% NMDEA/TMPTA

BBMQ = 2,3 Bis Bromomethylquinoxaline

DPQ = 2,3-Diphenylquinoxaline

DMQ = Dimethylquinoxaline

PQ = Styrylquinoxaline

DCQ = 2,3-Dichloroquinoxaline

DPQ/ACR = Diphenylquinoxaline/Acrylate

DMQ/ACR = Dimethylquinoxaline/Acrylate

Q/ACR = Quinoxaline/Acrylate

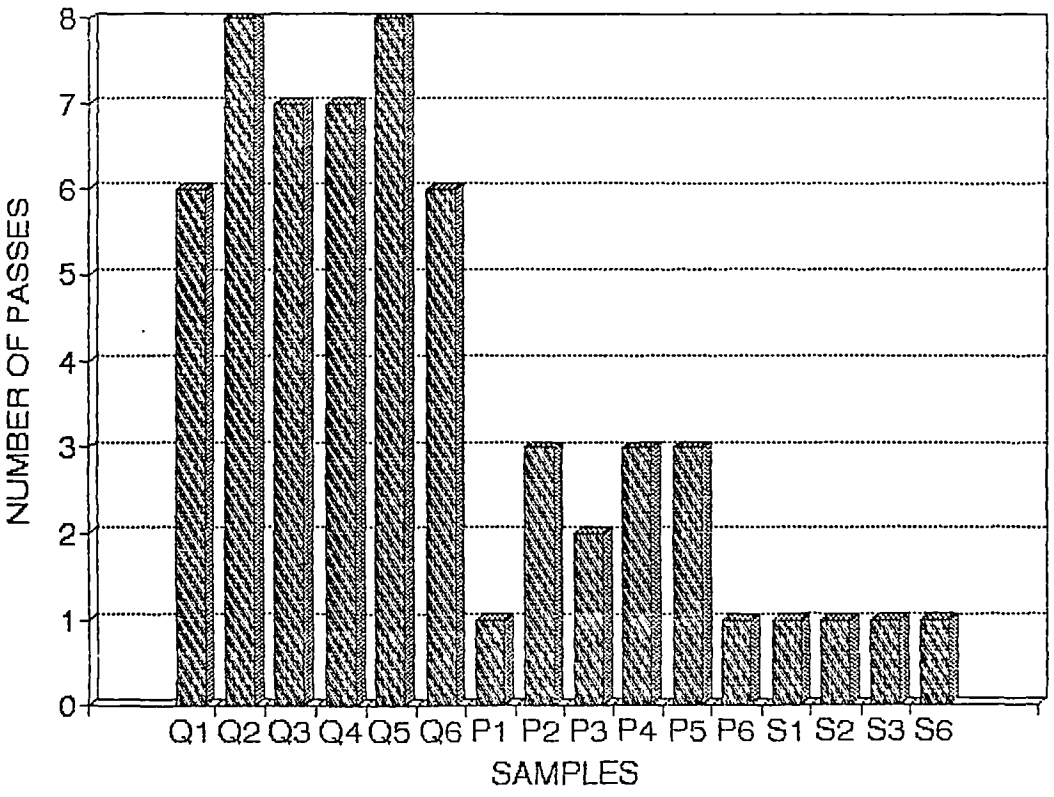


Fig. 3 .1 UV Curing Results of Various Quinoxalines

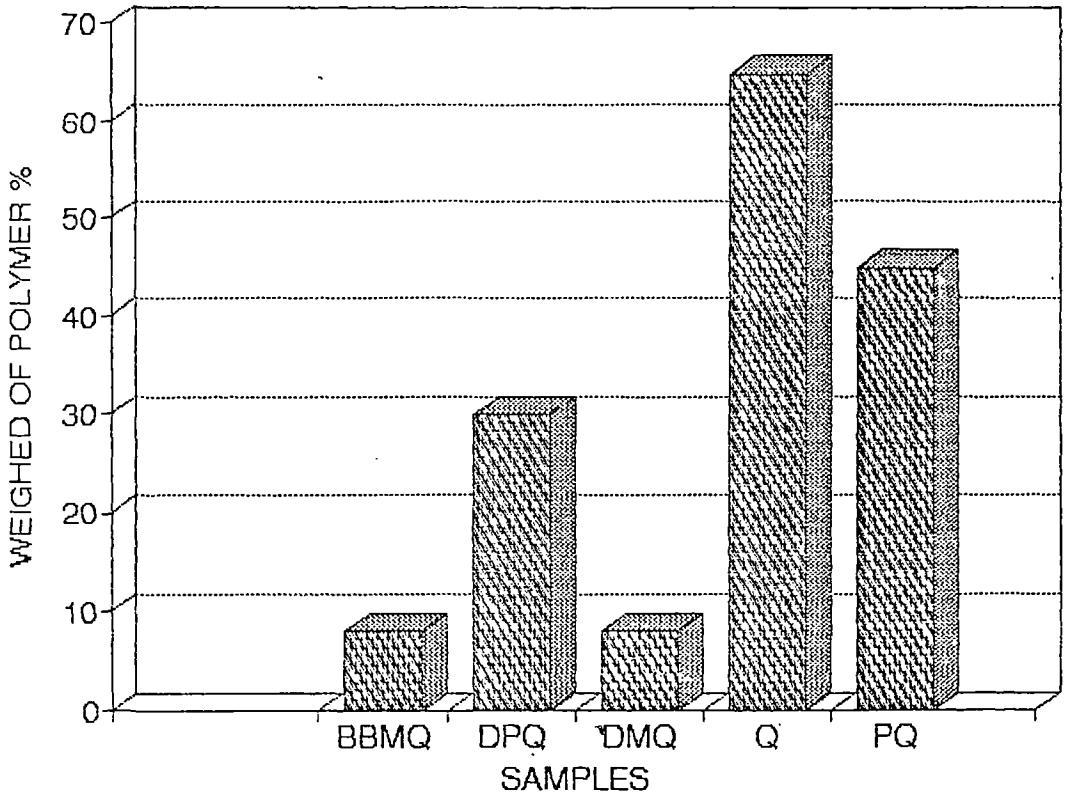


Fig. 3.2 Bulk Polymerisation Results of Various Quinoxalines

Oxidation of the reduced quinoxalines by molecular oxygen plays a part in the curing process as has been demonstrated by using the technique of Real Time Infrared Spectroscopy Irradiation was carried out in the presence and in the absence of air. The results are shown in Figs. 3.3 and 3.4 and Figs. 3.5 and 3.6, and the rate of polymerisation was also calculated as shown in Fig. 3.7 for the presence of air and in Fig. 3.8 for the absence of air.

As can be seen from Figs. 3.3 and 3.4, the cure of acrylate is faster when oxygen is present in the reaction mixture than when it is absent.

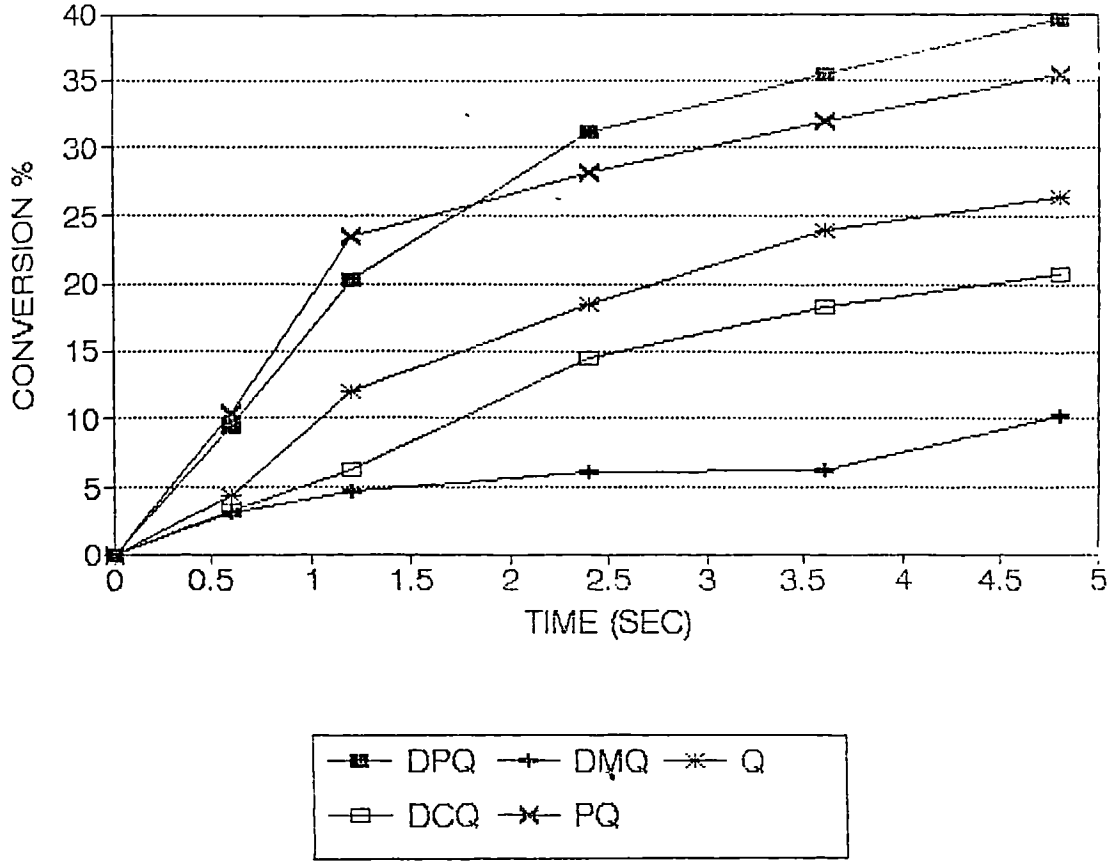


Fig. 3.3 Conv% of various Quinoxalines showing presence of air from RTIR Spectroscopy during 5 sec of irradiation

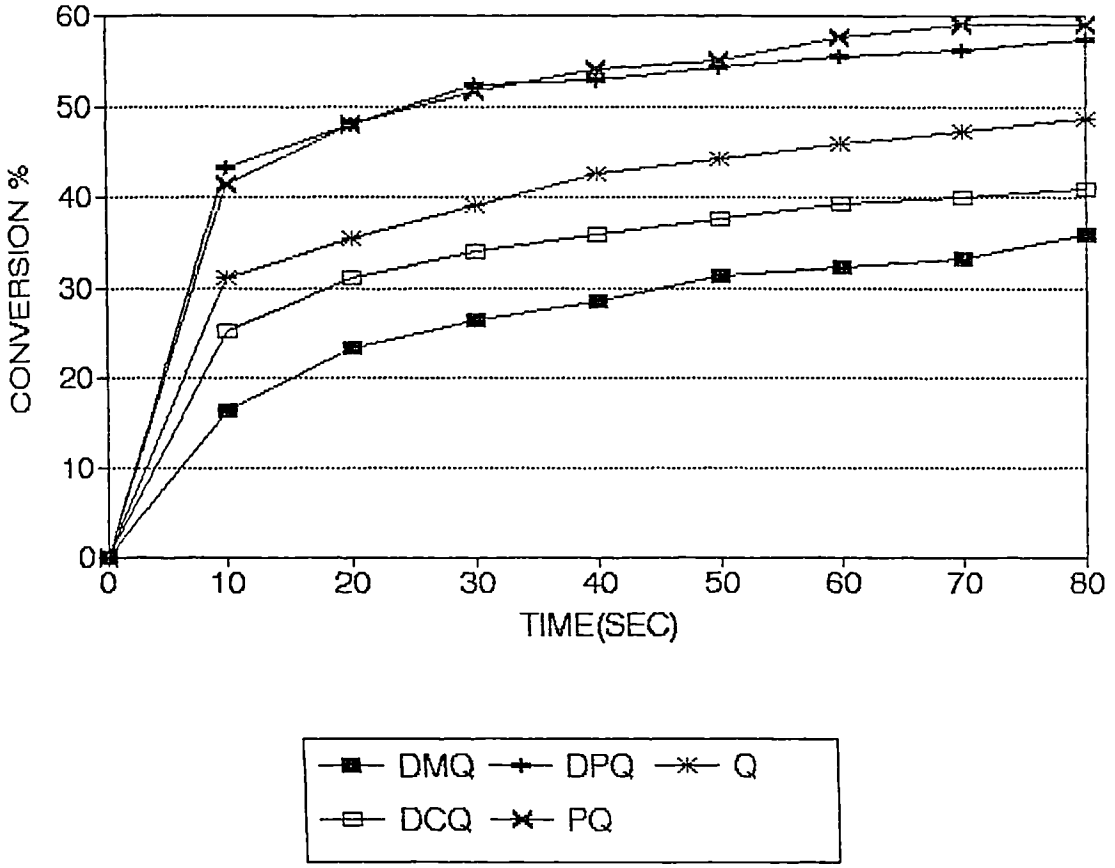


Fig. 3.4 Conv% of various Quinoxalines showing presence of air from RTIR Spectroscopy during 80 sec of irradiation

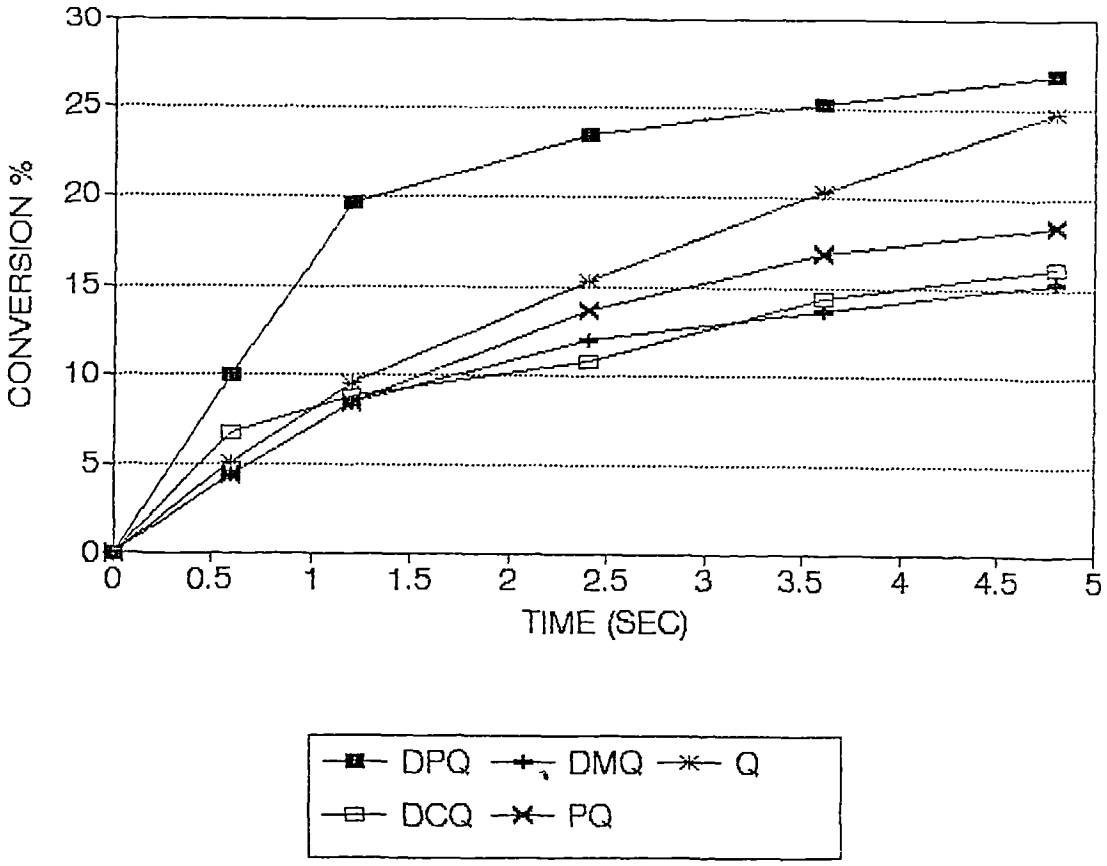


Fig. 3.5 Conv% of various Quinoxalines showing absence of air

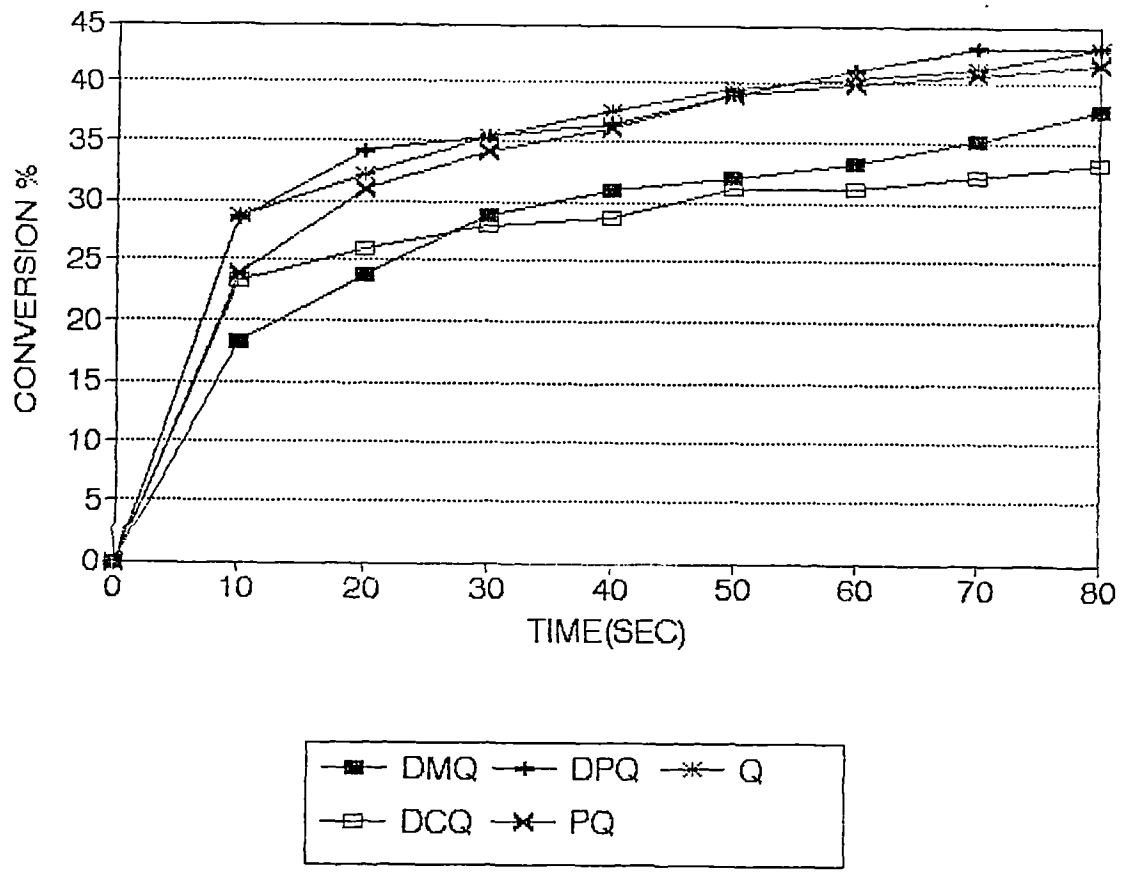


Fig. 3.6 Conv% of various Quinoxalines showing absence of air from RTIR Spectroscopy during 80 sec of irradiation

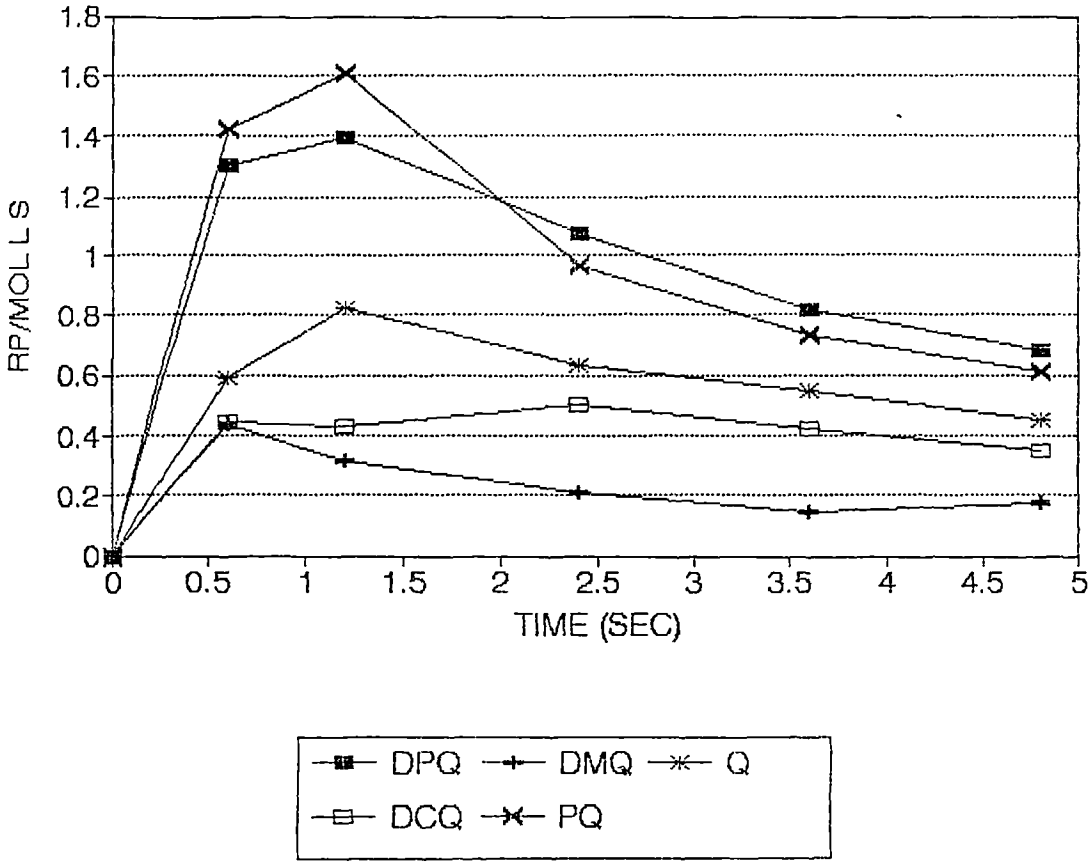


Fig. 3.7 The rate of polymerisation of various Quinoxalines in the presence of air

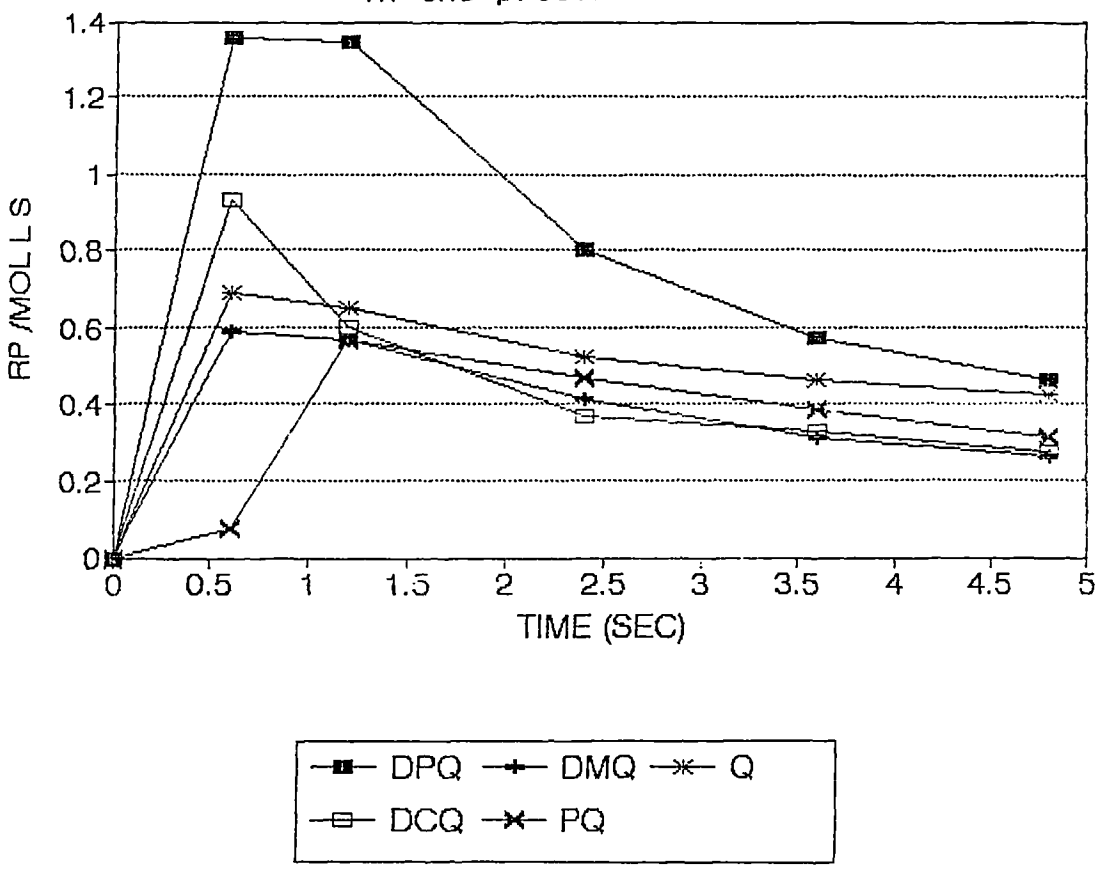


Fig. 3.8 The rate of polymerisation of various Quinoxalines in the absence of air

The polymerisation of TMPTA (trimethylolpropanetriacrylate) with quinoxalines in the absence of amine was also investigated and it was found that many of the quinoxalines initiated the polymerisation of acrylate in the absence of NMDEA, but oxygen inhibition of cure was very marked. Simply, in the present of air no cure was observed. The results are given in Figs. 3.9 and 3.10 and in the rates of polymerisation are shown in Fig. 3.11.

2,3-Diphenylquinoxaline was used to explore some new synergists to see if it was able to counteract the inhibitory effect of oxygen.

2-(N-Methyl-N-phenyl-amio)-1-phenylethanol (1) and 1-(4-methylthiophenyl)-2-methyl-2-(N-morpholino)propan-1-ol) (2) were tested as synergists for the curing of (TMPTA) 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate with 2,3-diphenyl-quinoxaline as photoinitiator.

The solubility was a problem for synergist (2) but these two aminoalcohols worked as well as N-methyldiethanolamine but none stood out as being far superior to the standard amine.

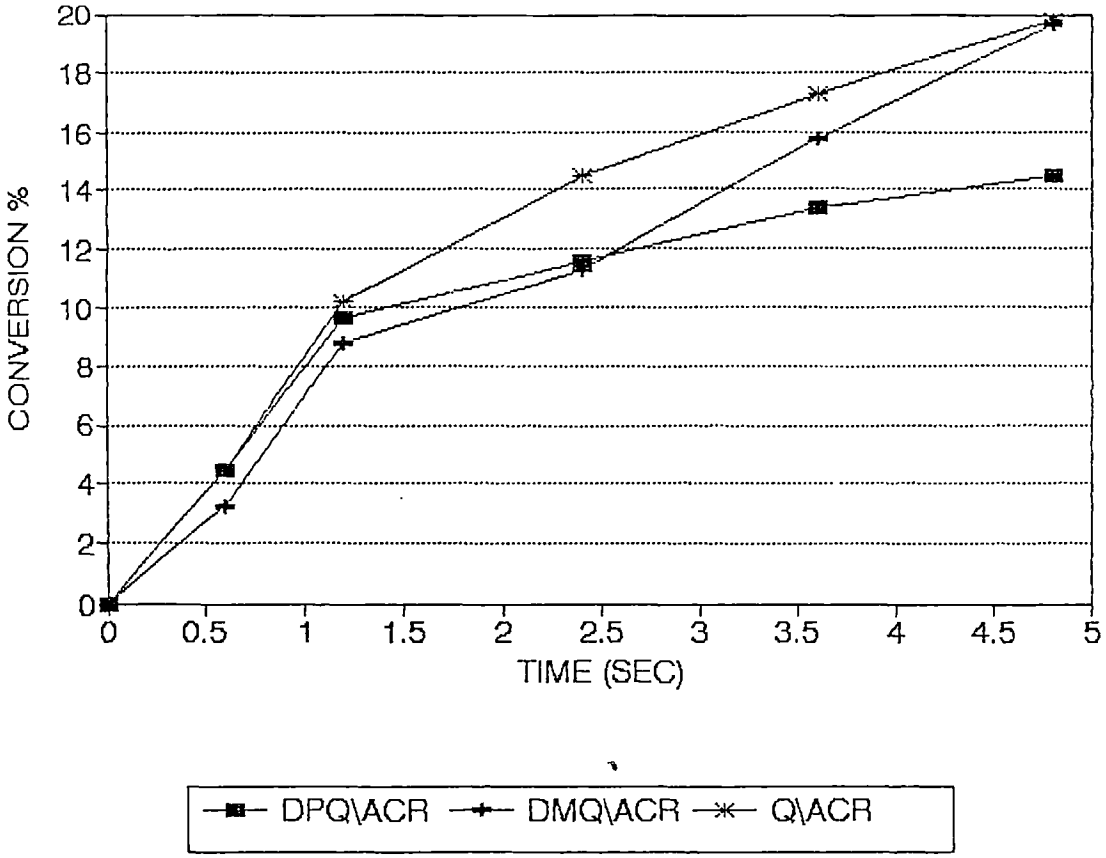


Fig..3.9 Conv% of various Quinoxalines without NMDEA in the absence of air from RTIR Spectroscopy during 5 sec irradiation

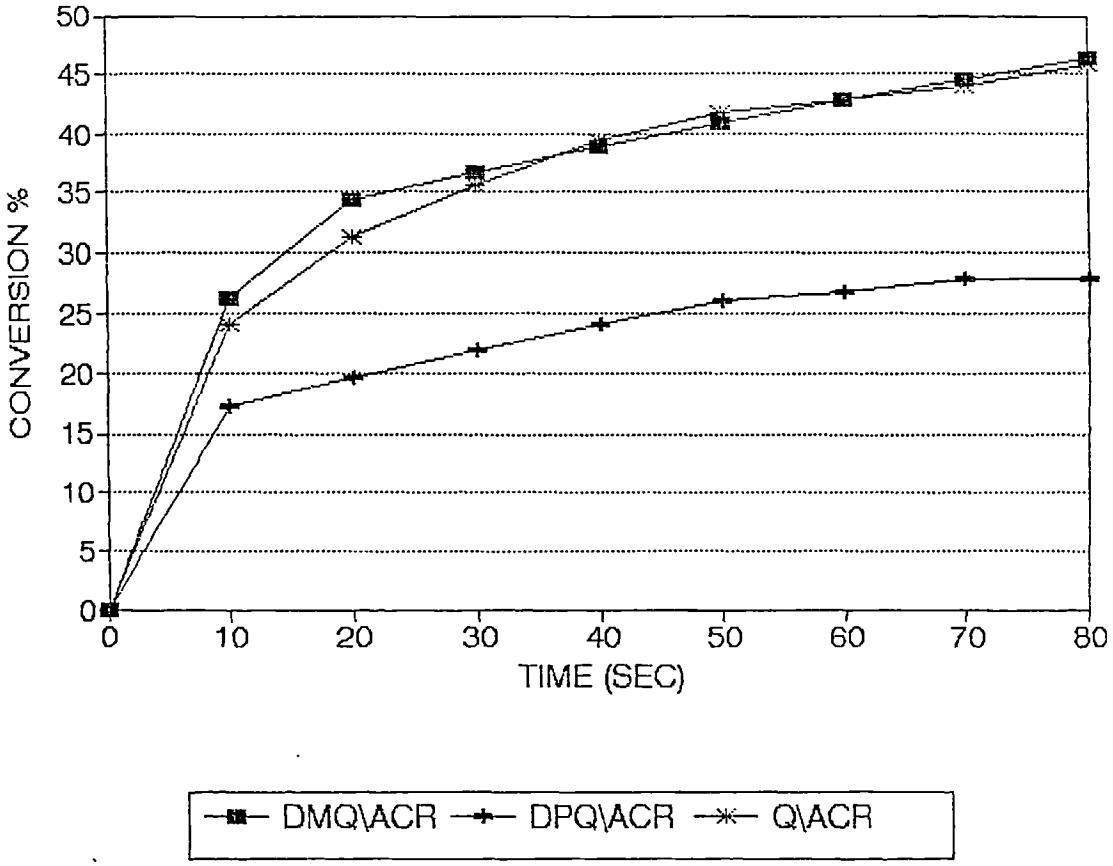


Fig..3.10 Conv% of various Quinoxalines without NMDEA in the absence of air from RTIR Spectroscopy during 80 sec irradiation

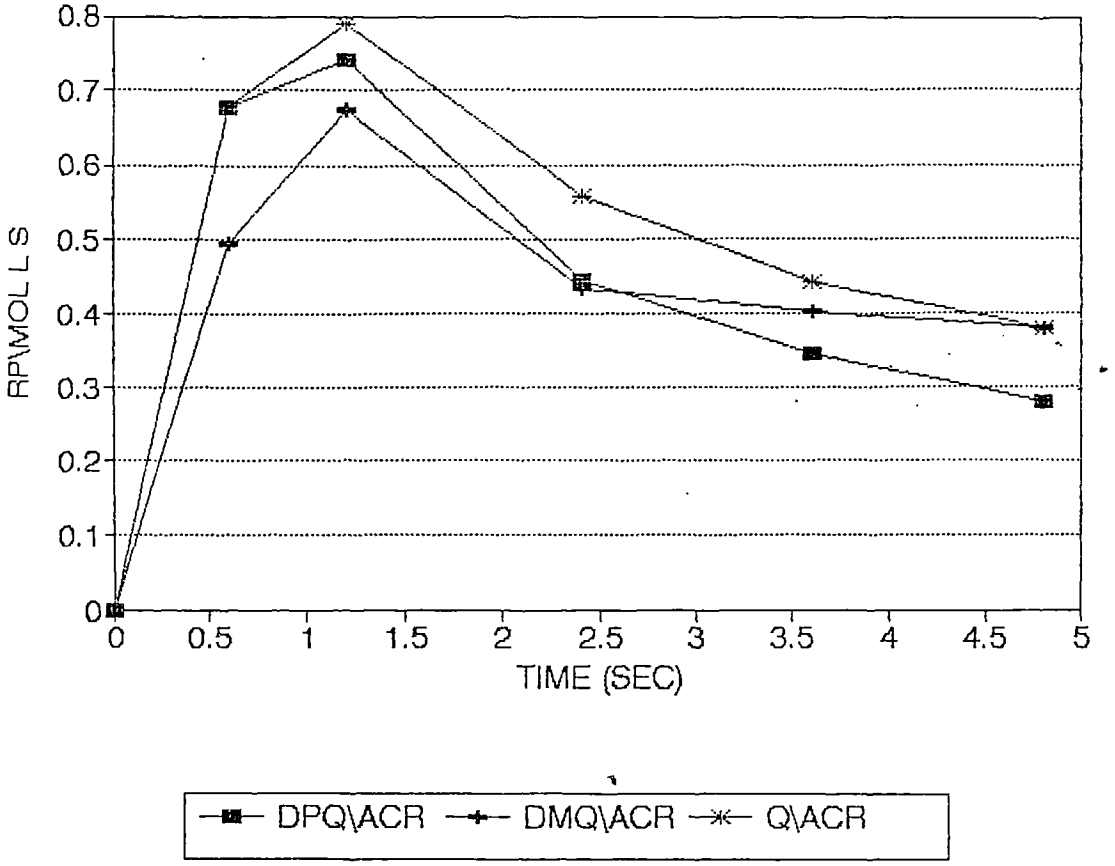


Fig. 3.11 The rate of polymerisation of various Quinoxalines without NMDEA and in the absence of air

The results for the quinoxalines in the mixtures Q1-Q6 (Fig. 3.1) show that when they are used at low concentrations and with a relatively small amount of amine, they act as initiators. As to what their real efficiency is, is hard to tell since each initiator possesses a different absorption spectrum and consequently each mixture will absorb a differing amount of light.

Increasing the initiator concentration through 1% (samples P1-P6) to 2% (samples S1-S6) leads in most cases (quinoxaline being the exception) to a gradual increase in the rate of cure. Quinoxaline was also shown to be an efficient initiator via

bulk polymerisation reactions. (Fig.3.2) with 2,3-diphenylquinoxaline performing relatively poorly.

These results are clearly at variance with the bulk polymerisation experiments but it should be remembered that the oxygen concentrations in the reaction mixtures for the two types of reaction are very different (lower oxygen concentration in bulk polymerisation) as shown in Fig.3.3 .

It can be seen that the aryl diphenylquinoxaline and styrylquinoxaline led to a reasonable percentage conversion of acrylate groups (for triacrylates the maximum amount of conversion is between 60-70%).

RTIR studies on the reaction mixtures from which oxygen has been removed show that a lower percentage conversion of acrylate groups is obtained (max 43% after 80 sec of irradiation).

Interestingly, the percentage conversion after 80 sec is reasonably similar for all the quinoxalines studied. This suggests that the variation in performance of the quinoxalines in aerated solution is in part due to the varying efficiency of oxygen induced regeneration of the quinoxalines from reduced and semi-reduced species.

The finding that quinoxalines in the absence of oxygen and amine initiator cause the cure of TMPTA backs up the previous claim that quinoxaline initiates the polymerisation of methyl methacrylate (23). Possibly if the acrylate had contained more readily abstractable hydrogen atoms (e.g. a polyether chain) the efficiency of polymerisation would be improved.

EXPERIMENTAL

UV curing of thin films was carried out using a Colordry UV Curing Unit. The medium pressure mercury lamp (100w/inch and 23 cm in length) was situated 15 cm above a moving belt which was calibrated in $mmin^{-1}$.

2,3-Diphenylquinoxaline, 2,3-dimethylquinoxaline and styryl quinoxaline were prepared by Dr Patricia Moran and 2,3-dichloroquinoxaline, 2,3-bis(bromomethylquinoxaline) and quinoxalines were obtained from Aldrich. Acenaphtho(1,2-b) quinoxaline and phenanthro [9,10-b] quinoxaline were prepared according to the method which was given in Chapter 2.

All samples were coated onto GNT papers by K-Bar. The thickness of the film was 12μ . The coatings were then passed under the UV lamp. The minimum number of passes required to produce a tack-free to the touch coating was recorded for a given belt speed. Conversion % and the rate of polymerisation were determined using RTIR kinetic cure which is mentioned in Chapter 4 . All solutions were coated on to a NaCl salt plate with 12μ K-Bar and replaced vertically on the IR sample plate holder and irradiated for 80 sec maximum.

For bulk polymerisation of trimethylolpropane triacrylate with quinoxalines, a general procedure was used which is: the photoinitiator (1%) was dissolved in acrylate (TMPTA) and N-methyldiethanolamine (10%) was added to the mixture and throughly mixed. The solution was irradiated in four Pyrex tubes (280 x 13 mm) and the tubes were rotated around a water cooled medium pressure mercury lamp (Hanovia, 100w/inch) over a timed period. Immediately following irradiation the polymer was taken by petroleum ether (boiling range 60-80^{o}. The precipitated polymer was collected on a pre-weighed sinter, washed with petroleum ether and dried in a vacuum desiccator until a constant weight was obtained.

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CHAPTER 4

PHOTOREACTIVITY OF IRG-907 COMPARED TO OTHER PHOTOINITIATORS

Chapter 4. PHOTOREACTIVITY OF IRG-907 COMPARED TO OTHER PHOTOINITIATORS

INTRODUCTION

Real-time infrared (RTIR) spectroscopy has been used to follow photopolymerisation processes in real time that take place in less than one second [1]. The technique allows the conversion of polymerisable monomer to be recorded directly as a function of the exposure time for reactions occurring within a fraction of a second. The rate of polymerisation as a function of photoinitiator concentration, and the % conversion were determined.

This method is well suited to study the effect on the polymerisation rate of the photoinitiator efficiency, the monomer reactivity, the effect of light intensity, the film thickness and of O_2 inhibition.

RTIR spectroscopy allows the important kinetic parameters to be evaluated in a single experiment. These are respectively:

The degree of conversion; this is directly related to the decrease of the IR absorbance, and can be calculated from the equation:

$$\text{Degree of conversion: } \frac{(A_{810})_o - (A_{810})_t}{(A_{810})_o} \times 100\%$$

The absorption peak at 810 cm^{-1} is characteristic of the acrylate group and is associated with the CH deformation mode [2,3].

$(A_{810})_o$ and $(A_{810})_t$ represent the absorbance at 810 cm^{-1} of the sample before and after UV exposure during time t. From these kinetic curves, one can readily evaluate how many acrylic bonds have polymerised.

The rate of polymerisation; (Rp) can be determined at any moment of the reaction from the slope of the RTIR kinetic curve.

$$Rp = [M]_o \frac{(A_{810})t_1 - (A_{810})t_2}{(A_{810})t_o \ (t_2 - t_1)}$$

t_1, t_2 = UV exposure times

Where $[M]_o$ is the concentration of acrylate double bonds before UV exposure. The quantum yield of polymerisation (^{Q}p) which corresponds to the number of functional groups polymerised per photon absorbed is calculated from the ratio of Rp to the absorbed light intensity.

$$Q_p = \frac{R_p = (mol^{-1}\ s^{-1})\ l\ (cm)}{10^3\ (1-e^{-2.3A})\ I_o\ (Einstein\ cm^{-2} s^{-1})}$$

Where A is the absorbance of the sample and l the film thickness. From Q_p values, the kinetic chain length (ν) of the polymerisation can then be evaluated, once the initiation quantum yield (Q_i) is known since $\nu = Q_p/Q_i$.

In the photopolymerisation of a multifunctional monomer (UV curing), where it is difficult to evaluate the molecular weight of the crosslinked polymer formed, quantum yield measurements appear to be the best method of evaluating the kinetic chain length of the reaction.

The induction period (t_i) which is observed only for experiments carried out in the presence of air, shows how effectively O_2 interferes with the polymerisation process. Whilst negligible in photocationic polymerisation, this inhibition effect was found to be of great importance in radical-induced polymerisations [2] which are most often carried out in thin films because of the limited penetration of UV radiation in organic materials. Because of the high surface area to mass this leads to good oxygen permeability.

The photosensitivity (S) of a UV-curable resin or resist is usually defined as the amount of energy which is required to polymerise half of the reactive functional group [3].

$$S = t_{0.5}Pf$$

where P is the radiant power incident on the sample, expressed in $mWcm^{-2}$, and f the fraction of light absorbed by the sample. The lower S value, the more sensitive the UV-curable system will be.

The residual unsaturation content (τ) of photopolymers can be quite important, especially for multifunctional monomer systems where polymerisation stops at an early stage as a consequence of the network formation and the resulting drop in the segmental mobility of the growing polymer chain.

$$\tau = [(A_{810})_t/(A_{810})_o]\ [M]_o$$

Its value has been found to be highly dependent on both the monomer functionality and the chemical structure of the functionalised oligomer chain [4].

PHOTOINITIATOR CONCENTRATION

From the rate equations presented in Chapter 1, where the rate of photoinitiation is directly proportional to the square root of the photoinitiator concentration [5], an increase in the level of photoinitiator would be expected to enhance the cure speed of the UV curable resin. Several reports claim that the cure rate and the degree of polymerisation of a formulation will at first increase with increasing photoinitiator concentration, and after passing through a

maximum or optimum concentration, this effect rapidly falls off [6,7,8,9-12]. This effect will largely depend upon the absorbance characteristics of the photoinitiator and that of the UV curable formulation. Significant changes in the rate of cure and the overall film properties are often observed for extremely thick or thin films [11].

For thin clear coatings(Fig 4.1)on a reflective substrate, a high proportion of the light entering the film will reach the substrate and will most probably cause multiple internal reflections within the film.

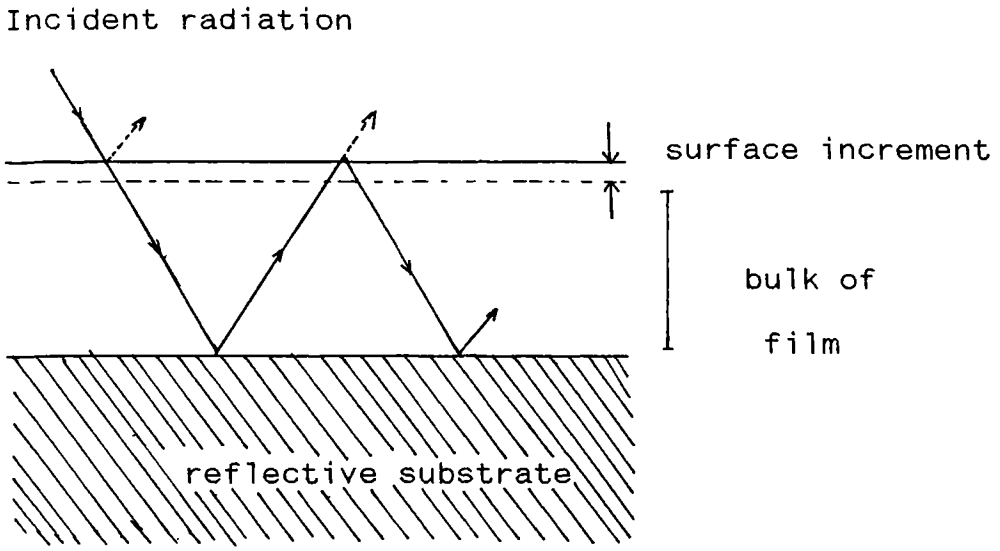


Fig 4.1 Reflection situation for thin clear films

The surface layer of the film will therefore receive a substantial amount of radiation which has been reflected from

the substrate. Consequently, the rate of surface cure is no longer a simple function of initiator concentration. Other factors, such as the film thickness, the substrate reflectivity and the refractive index of the vehicle are involved.

The relationship between the degree of polymerisation and the chemical nature of the photoinitiator/monomer system however, is more complicated and depends upon a variety of factors which include the quantum efficiency and the extinction coefficient of the monomer and photoinitiator side reactions. At higher photoinitiator concentrations the absorbance of UV light appears to generate a higher concentration of free radicals near the surface of the film. This higher concentration of photoinitiator and therefore free radicals at the surface is thought to block sufficient energy from penetrating the film, preventing photoactivation below a given thickness. Below this level an insufficient number of free radicals are generated in order to initiate and sustain the polymerisation process, and therefore the rate of polymerisation decreases. Photoinitiators which have a high molar extinction coefficient would be expected to give rise to this uneven distribution more readily than photoinitiators which have a low extinction coefficient and do not absorb UV light so strongly [8,11].

Increasing the photoinitiator concentration may result in a

point being reached at which so much light is absorbed in the upper regions of the film that through cure ceases to take place.

The effect of the monomer

The prime function of a monomer is to act as a solvent for the prepolymer by adjusting its concentration, amd controlling the viscosity of the formulation. It also acts as a crosslinking agent when polyfunctional monomers are used and determines the cure response of the system. The proportion of monomer present in a system is very important as this may affect film properties such as film hardness, flexibility, etc. The main classes of monomers are acrylates, vinyls and allylics and their cure response is in the order:-

Acrylic>methacrylic>vinyl>allylic

The cure response is also affected by the functionality of the monomer, i.e. the number of reactive groups per molecule and increases with increasing functionality [6,9,10,13].

OXYGEN INHIBITION

The ability of oxygen to inhibit photoinitiation and photopolymerisation has been described previously in Chapter 1. This effect, where polymerisable surface coatings are

concerned, can be very dramatic, requiring up to 20 times more energy to effect the same level of cure in the top 1μm of a clear film exposed to air compared to the 1μm layer 5μm below the surface [9]. The ability of oxygen to quench the excited states of the photoinitiator [16] and scavenge the initiating radicals [14] and the growing polymer radicals [15]. Furthermore, the formation of hydroperoxide is detrimental to the chemical and physical properties of the cured film [9,11].

While it has long been recognised that amines are effective synergists when used with benzophenone, or thioxanthone type photoinitiators, it has been shown [6,14] that certain amines can be used with cleavage type photoinitiators to accelerate the cure rate in an air atmosphere. This presumably occurs as a result of the generation of a radical species capable of oxygen scavenging by a radical chain process, as shown in Scheme I.

$$PI + h\nu \longrightarrow R. \quad (1)$$

$$R.(\text{or } P.) + R_2'NCH_2R'' \longrightarrow RH(\text{or } PH) + R_2'\dot{N}CHR'' \quad (2)$$

$$R.(\text{or } P.) + O_2 \longrightarrow ROO\cdot(POO\cdot) \quad (3)$$

$$ROO\cdot(\text{or } POO\cdot) + R_2'NCH_2R'' \longrightarrow ROOH \text{ (or } POOH) + R_2'\dot{N}CHR'') \quad (4)$$

$$R_2'\dot{N}CHR'' + O_2 \longrightarrow R_2'N\overset{OO\cdot}{\underset{|}{C}}HR'' \quad (5)$$

$$R_2'N\overset{OO\cdot}{\underset{|}{C}}HR'' + R_2'NCH_2R'' \longrightarrow R_2'N\overset{OOH}{\underset{|}{C}}HR'' + R_2'\dot{N}CHR'' \quad (6)$$

Scheme I

Where PI is the photoinitiator, R is the primary radical and P is the polymer radical. The amine radical generated in this chain process can serve either to initiate polymerisation or to combine with additional molecules of oxygen. The detrimental effect of chain transfer to amines can be avoided by incorporating the amine functional groups into monomers which themselves are capable of participating in the polymerisation process [14].

While the addition of amine serves to increase the cure rate of polymerisation and lower the substantial differences between through cure and surface cure (caused by oxygen inhibition), the hydroperoxides (POOH) that accumulate during propagation (Scheme I, equations 3, 4) will sensitise the photodegradation of the coating [15].

RESULTS & DISCUSSION

Effect of Chemical Parameters

The influence of the resin constituents on the kinetic parameters can be readily evaluated by RTIR spectroscopy which appears as an ideal tool for assessing the efficiency of new photoinitiators and monomers.

a) INFLUENCE OF THE PHOTOINITIATOR

A very important constituent in a UV curable formulation is certainly the photoinitiator, since even the most reactive acrylate monomers hardly polymerise when exposed in pure form to UV light [17]. It also governs the depth of penetration by radiation, and thus the depth of cure, which is directly related to the concentration of photoinitiator. Different photoinitiators, Type I and Type II were investigated by using RTIR spectroscopy. Determination of conversion of polymerisation and the rate of polymerisation were calculated from RTIR spectrum curves 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (Irg 907), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (Irg 369) 2,2-dimethoxy-2-phenylacetophenone (Irg 651). Isopropylthioxanthone (ITX) and benzophenone (BP) and 1-chloro-4-propoxythioxanthone (CPTX) were chosen as photoinitiators.

The formulations were prepared using the carbamate monoacrylate CL-960, tripropylene glycoldiacrylate (TPGDA) and acrylated epoxidised oil Photomer 3005. The samples were irradiated for 80 sec.

The formulations are as follows.

A1: 5% ITX
47.5% CL-960
47.5% P.3005

A2: 5% BP
47.5% CL-960
47.5% P.3005

A3: 5% Irg. 369
47.5% CL-960
47.5% P.3005

A4: 5% Irg.651
47.5% CL-960
47.5% P.3005

A5: 5% Irg. 907
47.5% CL-960
47.5% P.3005

In some cases amine was omitted so that comparisons could be made which showed the influence of amine.

Similar formulations were prepared using TPGDA instead of CL-960. The results are shown in Fig.4.2 and Fig.4.3 respectively for CL-960 and TPGDA for 5 sec of irradiation time When irradiation was prolonged to 80 sec, conversion percentages were calculated and shown in Fig.4.4 and Fig.4.5 respectively for CL-960 and TPGDA.

For fast UV-curable systems 50% conversion was reached within less than 1.5 sec of exposure. The rate of polymerisation was calculated for each system and shown in

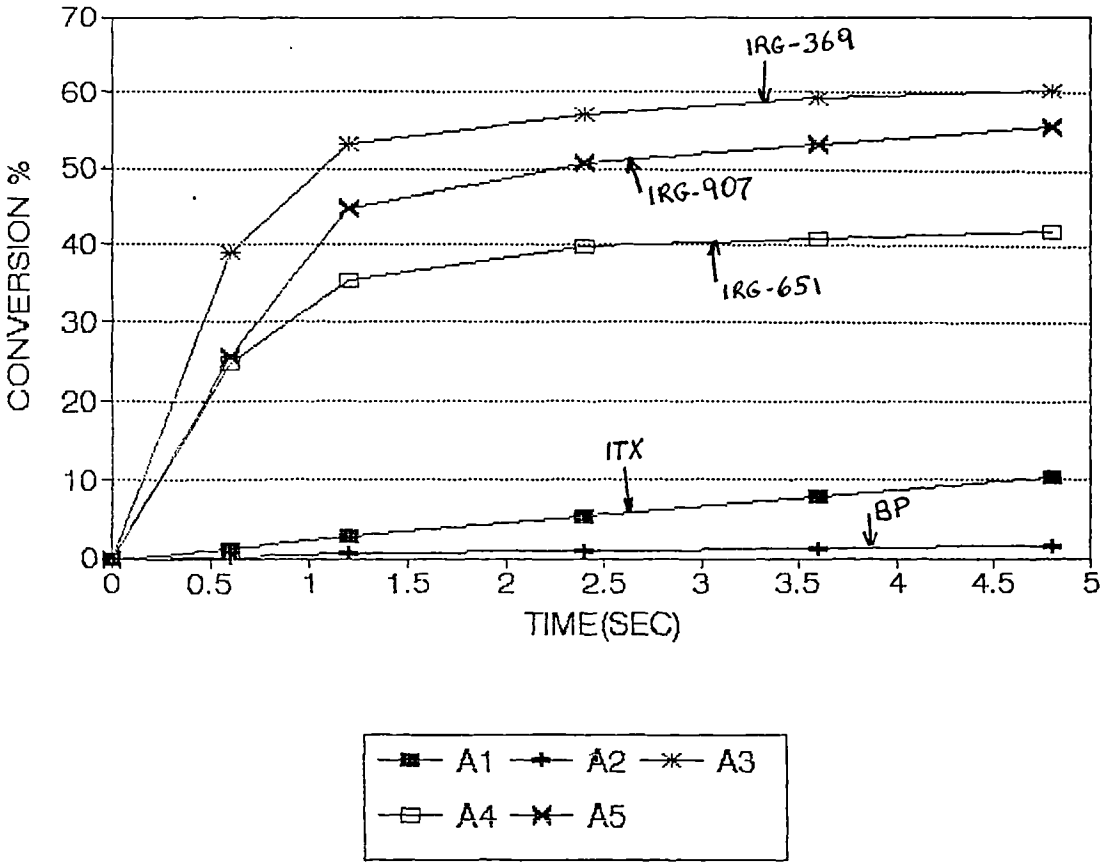


Fig 4.2. Conversion % of samples (A1-A5) in CL-960 showing from RTIR during 5 sec of irradiation.

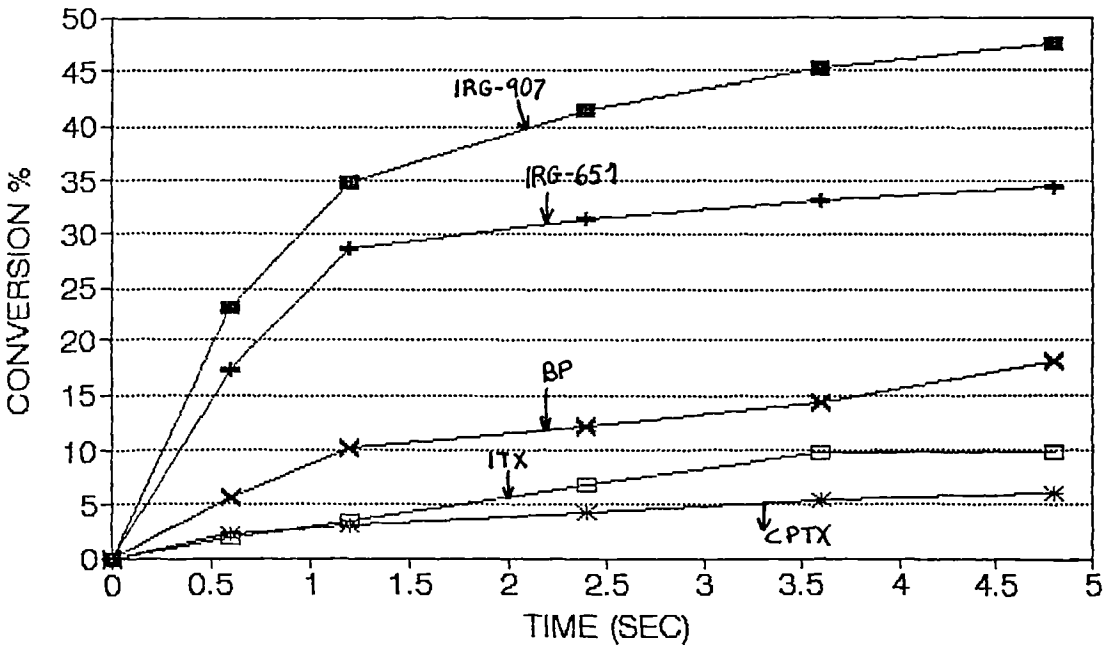


Fig 4.3 Conversion % of samples in TPGDA showing from RTIR during 5 sec of irradiation.

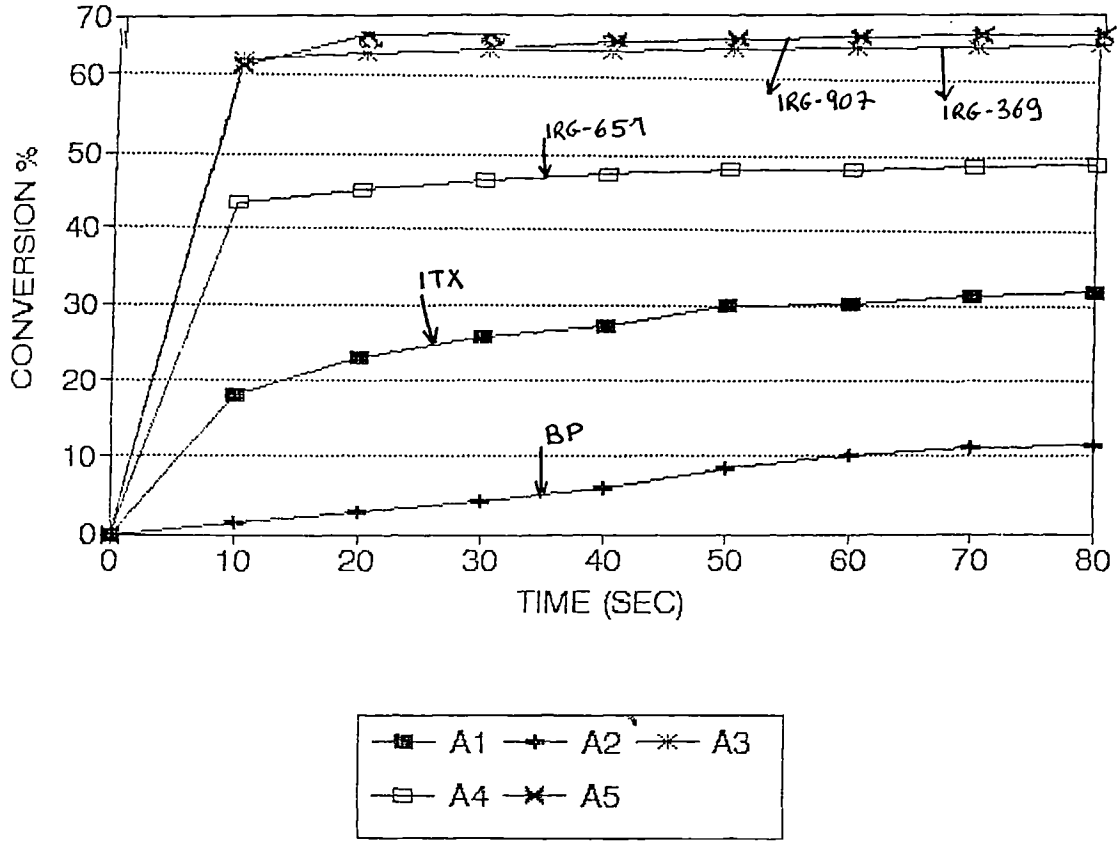


Fig 4.4. Conversion of samples (A1-A5) in CL-960 showing from RTIR during 80 sec of irradiation.

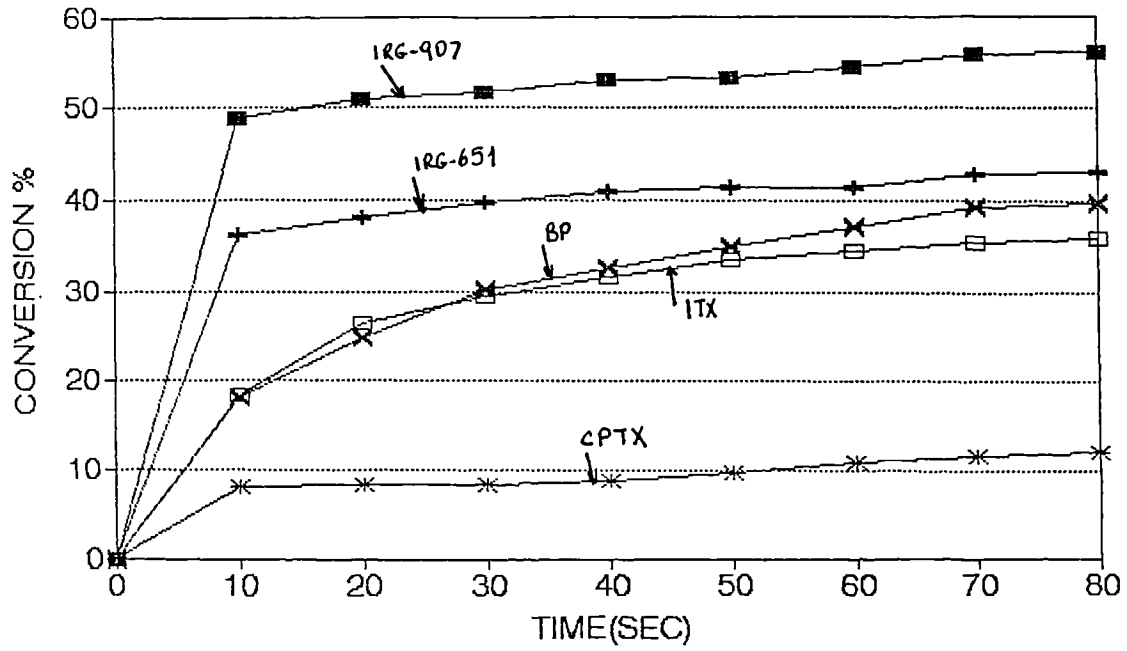


Fig 4.5. Conversion % of samples in TPGDA showing from RTIR during 80 sec of irradiation.

Fig.4.6 and Fig.4.7.

2-Benzyl-2-dimethyl-amino-1-(4-morpholinophenyl)-butan-1-one (Irg-369) led to 61% conversion of the double bonds. The conversion produced by using Irg-907 during a similar period of time (4.8 sec) was 56%.

When TPGDA was used in place of CL-960 with Irg-907 the percentage of conversion of double bonds was found to be slightly lower (Fig.4.5).

(b) INFLUENCE OF THE PHOTOINITIATOR CONCENTRATION

The concentration changes during irradiation of an initiator is another important factor which influences the photopolymerisation process. The effect of photoinitiator concentration was investigated using RTIR. 2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (Irg 907) was chosen as model photoinitiator and the effect of the concentration of Irg 907 was followed using RTIR spectroscopy.

The formulations were prepared starting from 2%, 4% and 5%. Monomer, CL.960 was used in P.3005 acrylated epoxy as the resin system. Conversions and the rate of polymerisation were determined from the RTIR results and shown in Figs.4.8, 4.9, and 4.10.

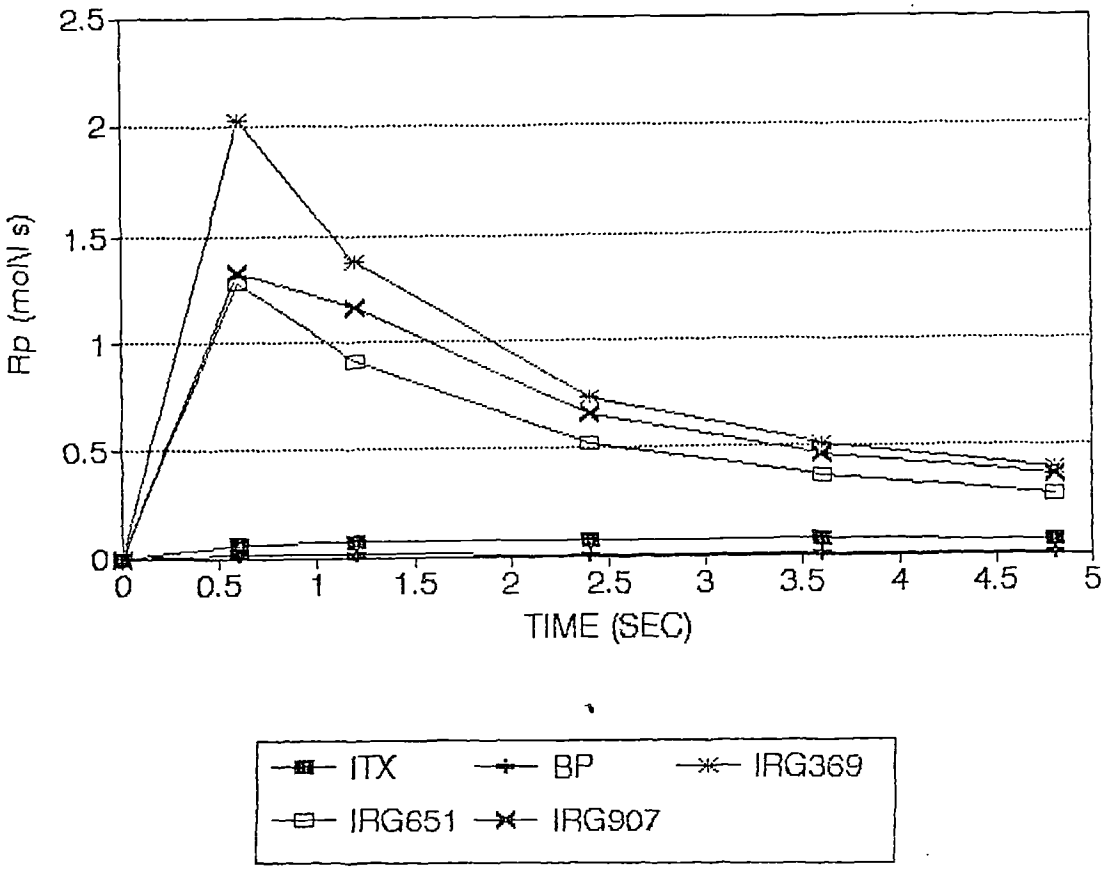


Fig 4.6. The rate of polymerisation of different initiators in CL-960.

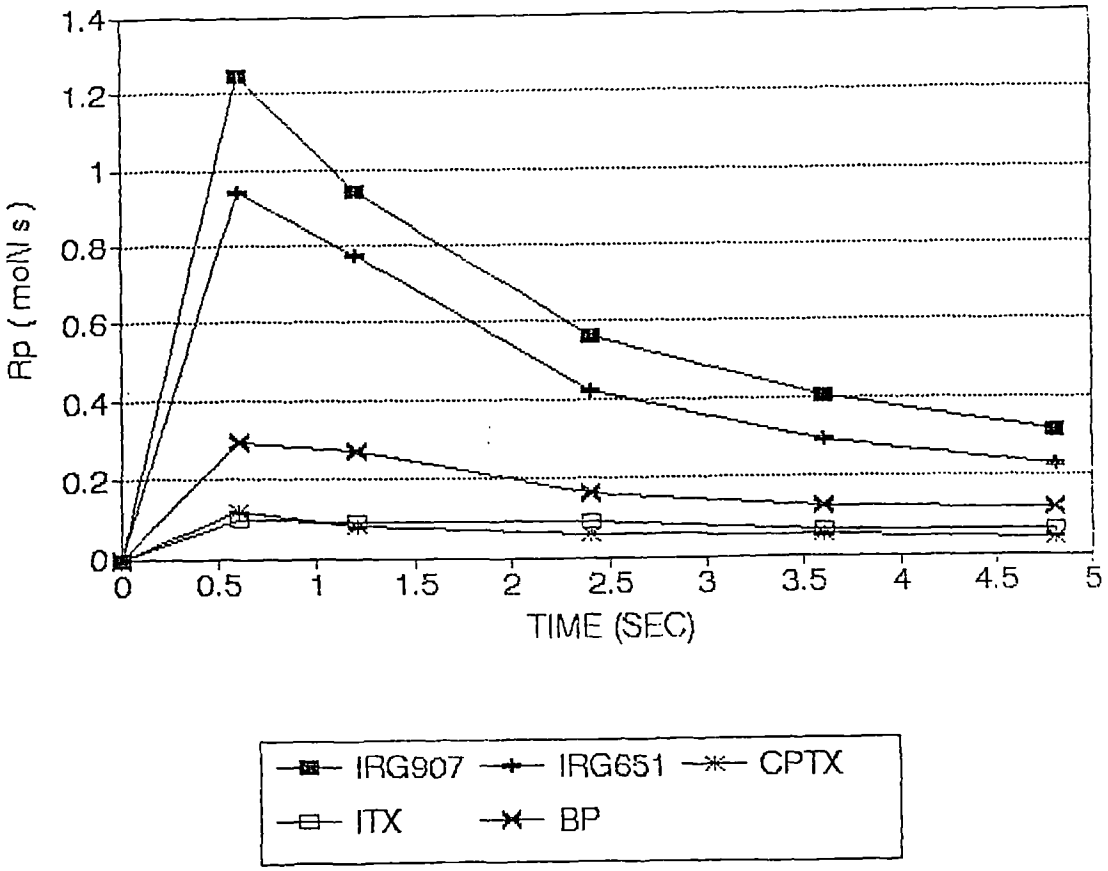


Fig 4.7. The rate of polymerisation of different initiators in TPGDA.

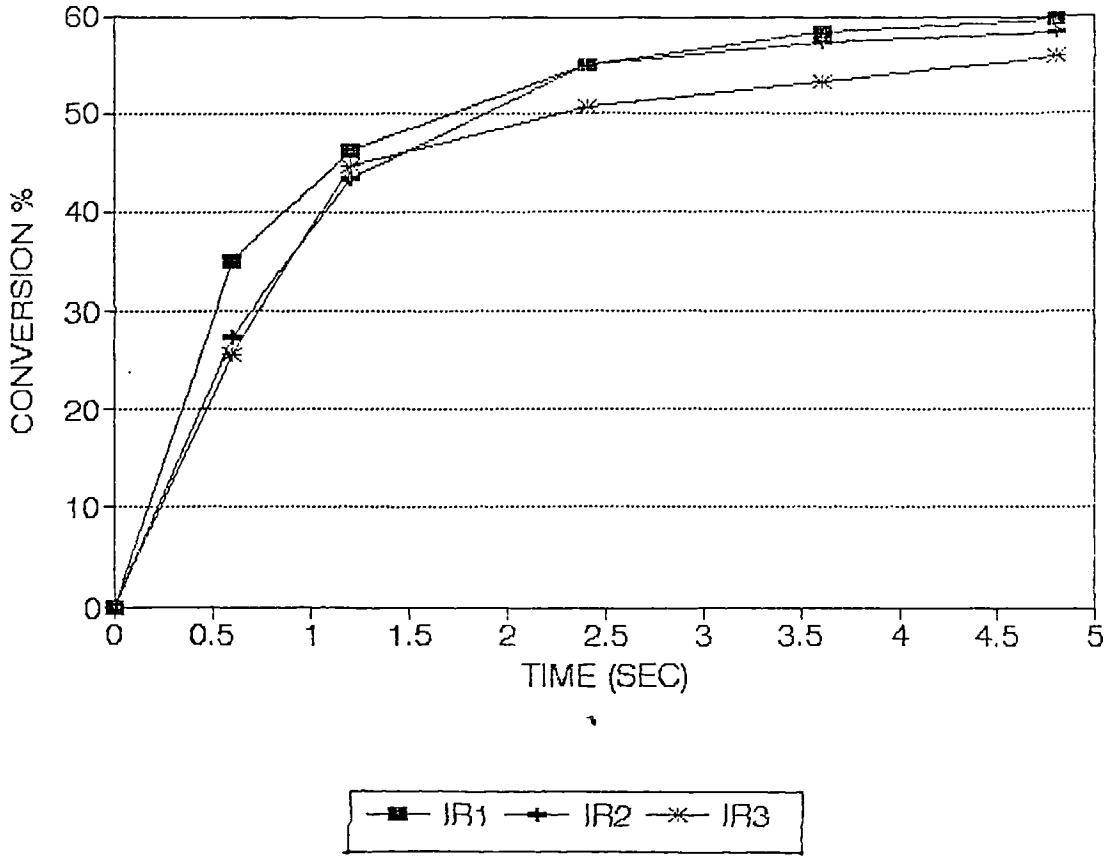


Fig 4.8. Conversion % of different concentration of Irg-907 in CL-960 showing from RTIR during 5 sec of irradiation.

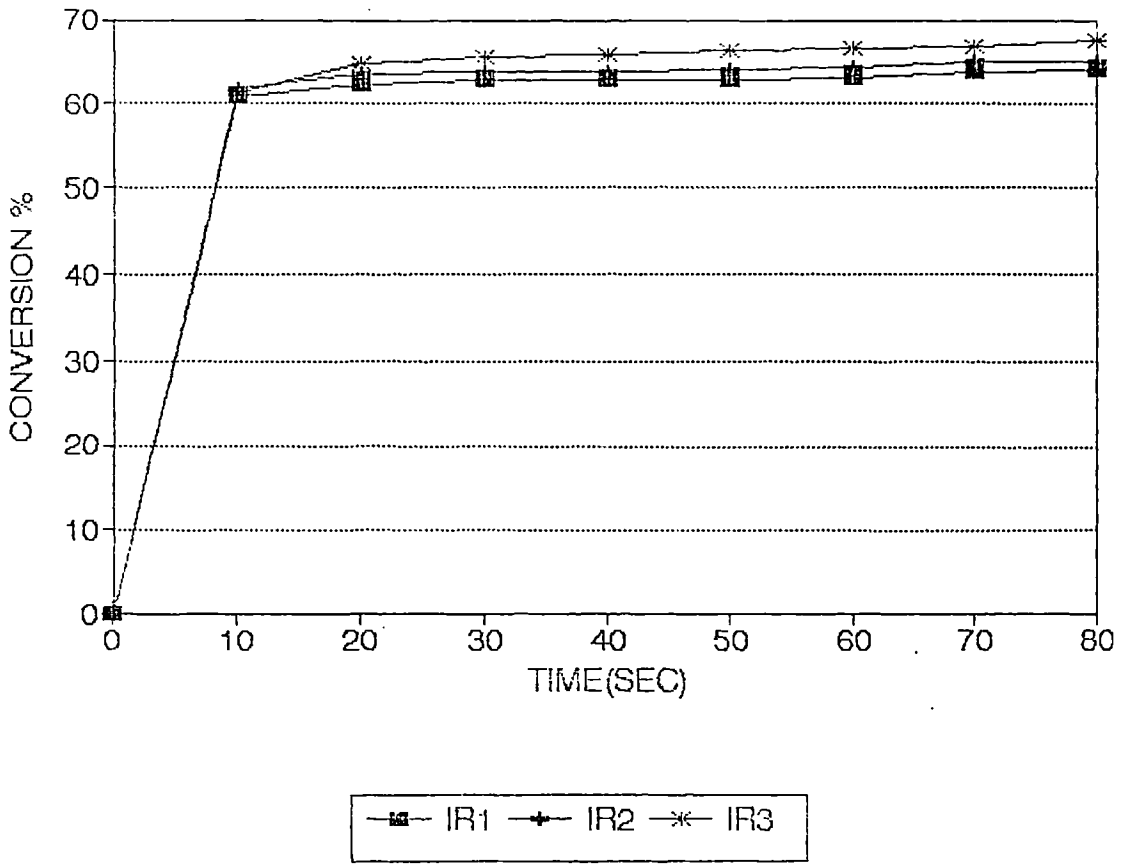


Fig 4.9. Conversion % of different concentration of Irg-907 in CL-960 showing from RTIR during 80 sec of irradiation.

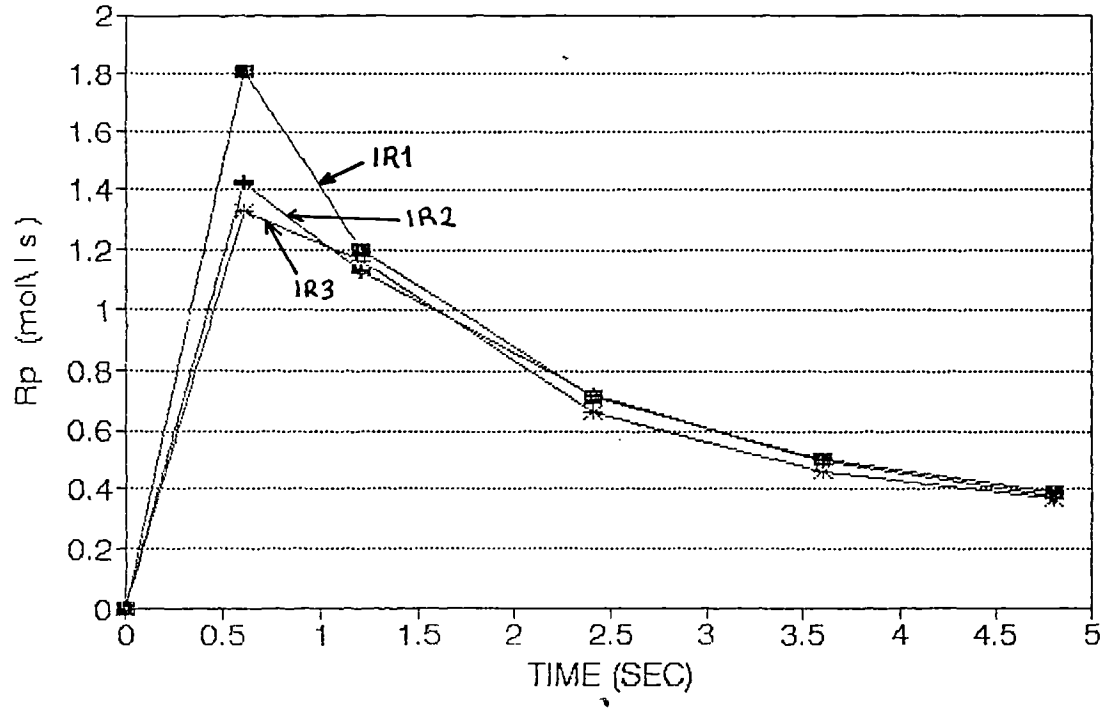


Fig 4.10. The rate of polymerisation of different concentration of Irg-907 in CL-960 .

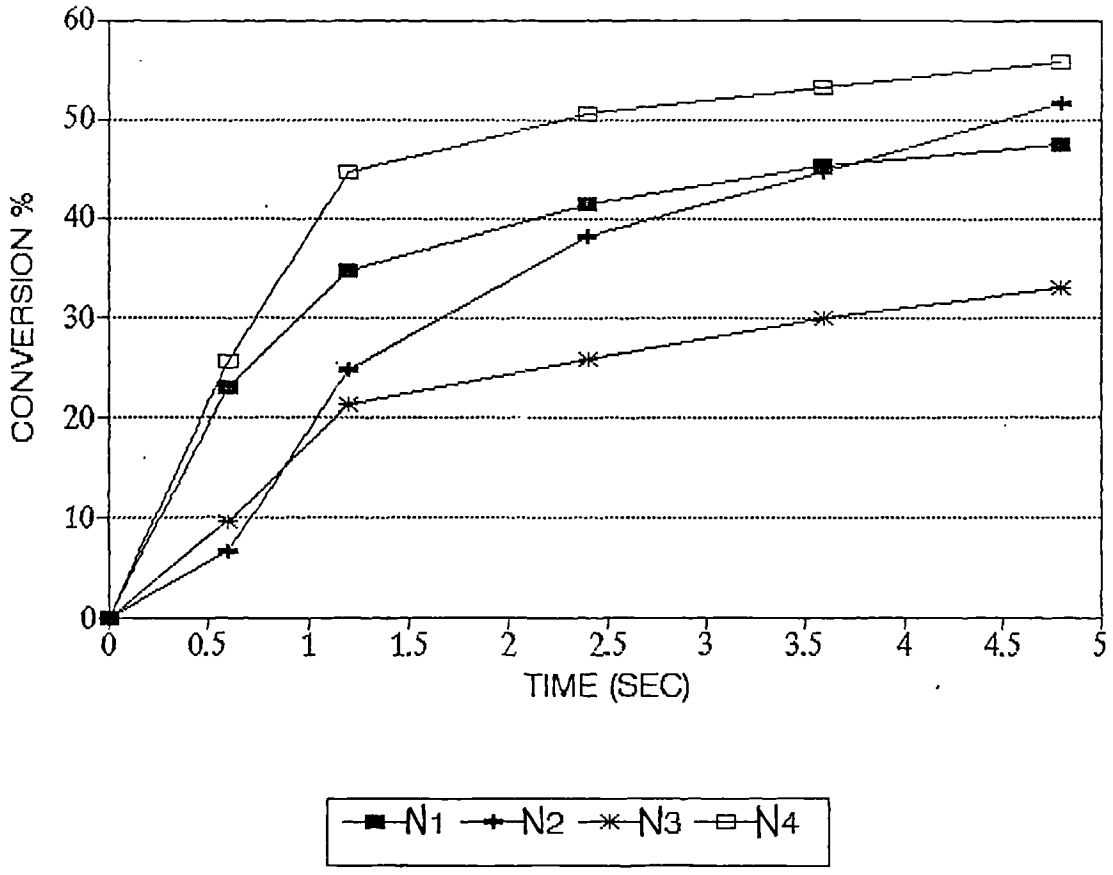


Fig 4.11. Conversion of 5% Irg-907 in different monomer systems showing from RTIR during 5 sec of irradiation.

Increasing the photoinitiator concentration from 2% to 4% and to 5% has not increased the cure speed of the system. During 0.5 sec of polymerisation 2% of Irg-907 had highest conversion which was 36% compared to 28% for 4% Irg-907 and 26% for 5% Irg-907 (Fig.4.8). Further conversion of acrylate groups occurred up to 10 secs irradiation and thereafter the percentage change was very small (Fig.4.9) The results were slightly at variance from each other. Conversions were 64% for 2% Irg-907, 65% for 4% Irg-907, and 67% for 5% Irg-907.

From these results, it can be seen that an increase in the photoinitiator concentration does not lead to an increase in the rate of polymerisation during 10 sec exposure to UV. High concentrations of photoinitiator may lead to absorption of light in the upper region of the film which decreases the rate of polymerisation due to radical termination. Also if the light does not penetrate the whole of the film radical production will not occur in all of the polymerisable material.

(c) INFLUENCE OF THE MONOMER

The monomer functionality has a marked effect on both the rate of polymerisation and the maximum conversion.

The following trend has been observed [3] for the various

acrylic monomers examined, in both epoxy-acrylate and polyurethane acrylate coatings:

reactivity : mono<di<tri

maximum conversion : tri<di<mono

In the presence of Irg-907, acrylic monomers were shown to polymerise readily under UV exposure (Fig.4.12). With the carbamate monoacrylate (Acticryl CL.960), 50% conversion was *reached within 2.4 sec of exposure in an air atmosphere* (Figs.4.11 and 4.12).

TPGDA, HDDA, CL.960 and CL.959 were used to show the effect of monomer functionality on the rate of polymerisation and the maximum conversion. The rate of polymerisation results are shown in Fig.4.3 and Table 1.

It should be stressed that the monomer Acticryl CL.960 which contains only one acrylate function exhibits a unique behaviour upon UV radiation; it polymerises more rapidly than a diacrylate and as extensively as monoacrylate [1,3].

N1: 5% IRG-907/ TPGDA

N2: 5%IRG-907/CL-959

N3: 5%IRG-907/HDDA

N4: 5%IRG-907/CL-960

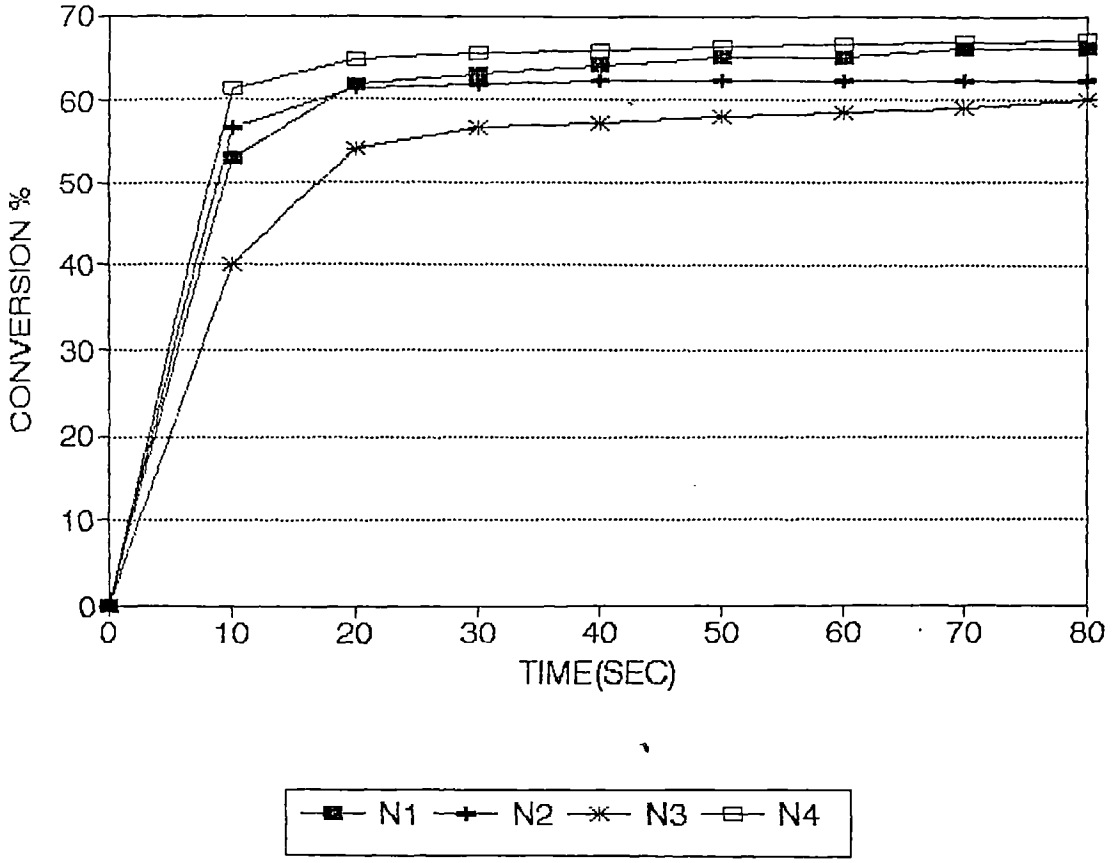


Fig 4.12. Conversion % of 5% Irg-907 in different monomer systems showing from RTIR during 80 sec of irradiation.

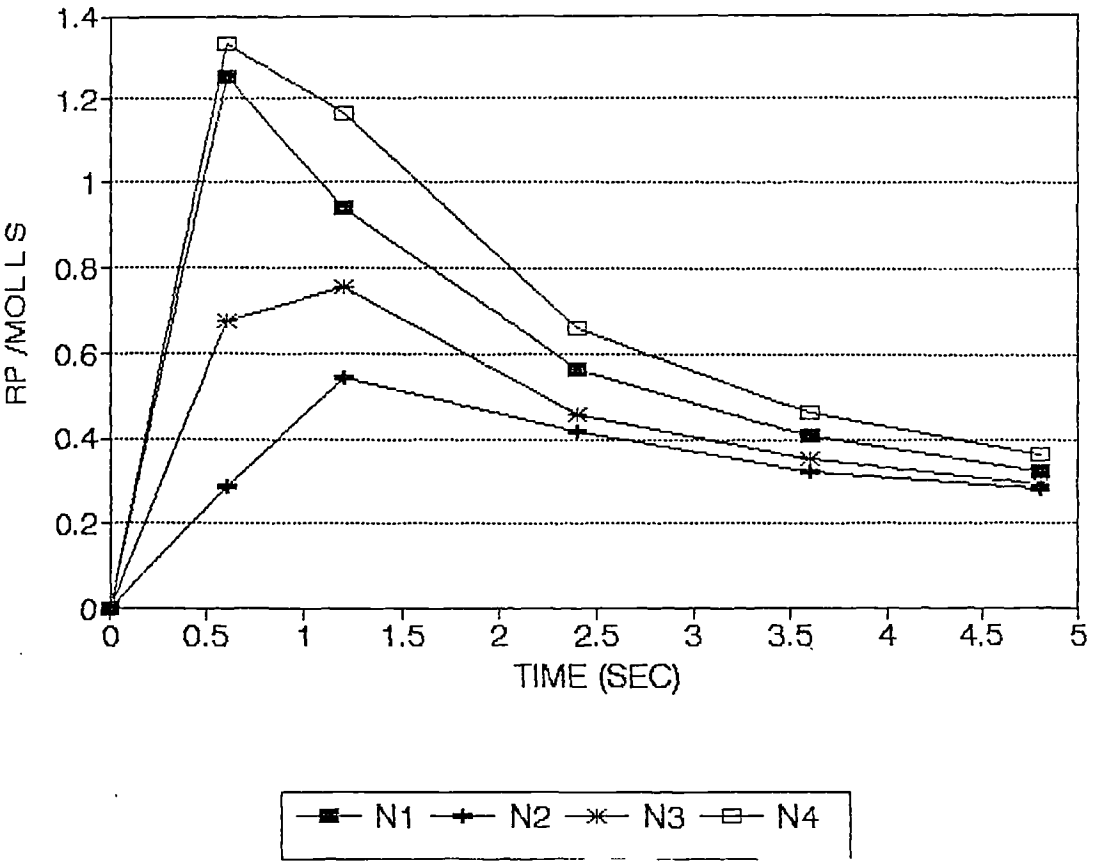


Fig 4.13. The rate of polymerisation 5% Irg-907 in different monomer systems.

Monomer	<Acrylate>/mol l^{-1}	Rp/mol $l^{-1}s^{-1}$
Monacrylate		
CL-959	2.62	0.286
CL-960	3.12	1.329
Diacrylate		
TPGDA	3.25	1.248
HDDA	4.24	0.674

Table 1

Results of photopolymerisation an acrylated epoxide P.3005 wt ratio P.3005/monomer 50:50 Irg 907 content 5wt% irradiation time 84 sec.

(d) EFFECT OF AMINE SYNERGIST

Tertiary amines are added to UV curing formulations in order to ameliorate the inhibiting action of atmospheric oxygen and in the case of Type II photoinitiator, to generate initiating radicals.

Tertiary amines are invaluable in reducing the concentration of oxygen with films thereby enabling the polymerisation process to take place efficiently [18]. Different types of photoinitiators were used to investigate the effect of amine synergist. Type I and Type II photoinitiators were investigated and the results are shown in Figs.4.12 and 4.13. Isopropylthioxanthone,1-chloro-4-propoxythioxanthone showed enhanced reactivity presence of amine synergist. Type I photoinitiators showed similar reactivity. Irg-907 which could possibly undergo reduction by the amine to give initiator radical does not show substantial increase in reactivity and therefore in all probability the initiation is via the Type I process. The same approach would apply for Irg 369 and Irg-651.

The effectiveness of amines as a synergist and reduction of oxygen inhibition lies in the reactivity of the C-H to the nitrogen atom [13].

Many tertiary amines are characterised by having low ionisation potentials with those of aromatic amines being generally lower than those of aliphatic amines.

For amines to act as synergists, a feature of great importance is the ease with which in either the exciplex or in reactions

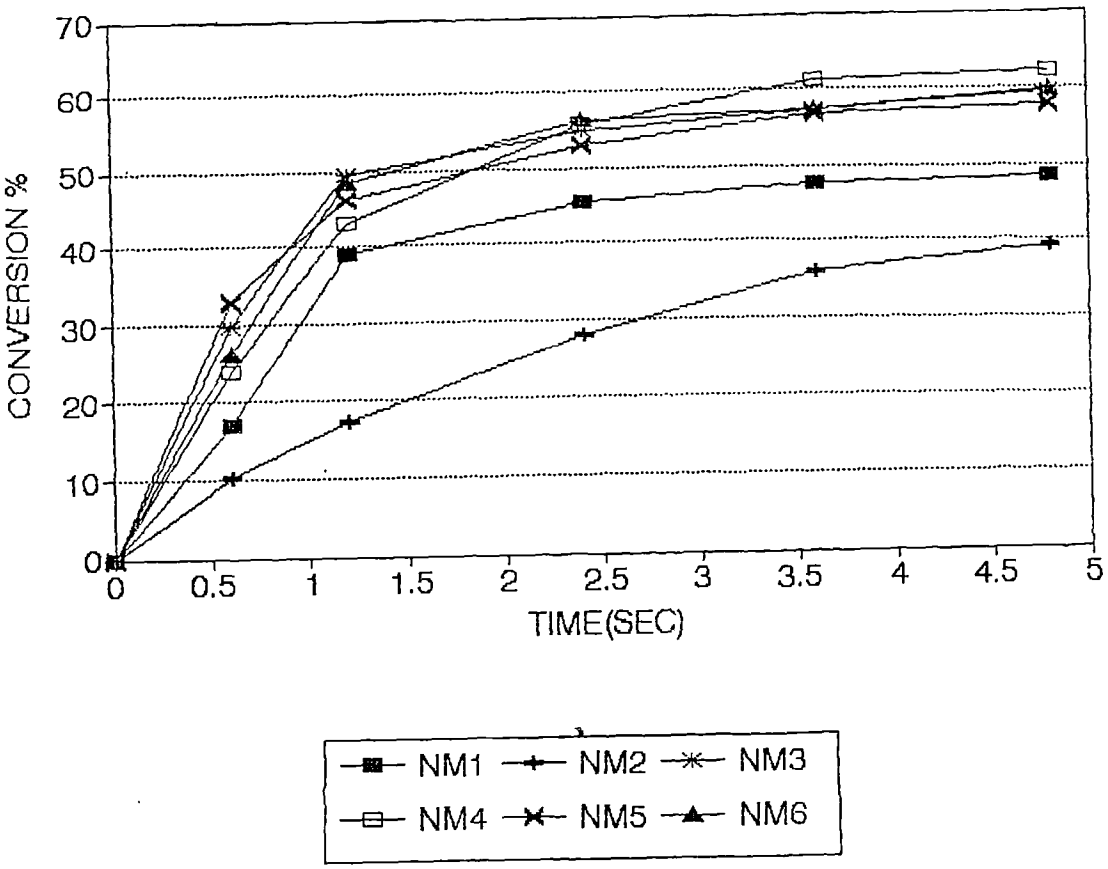


Fig 4.14 . Conversion % of samples (NM1-NM6) showing from RTIR during 5 sec of irradiation.

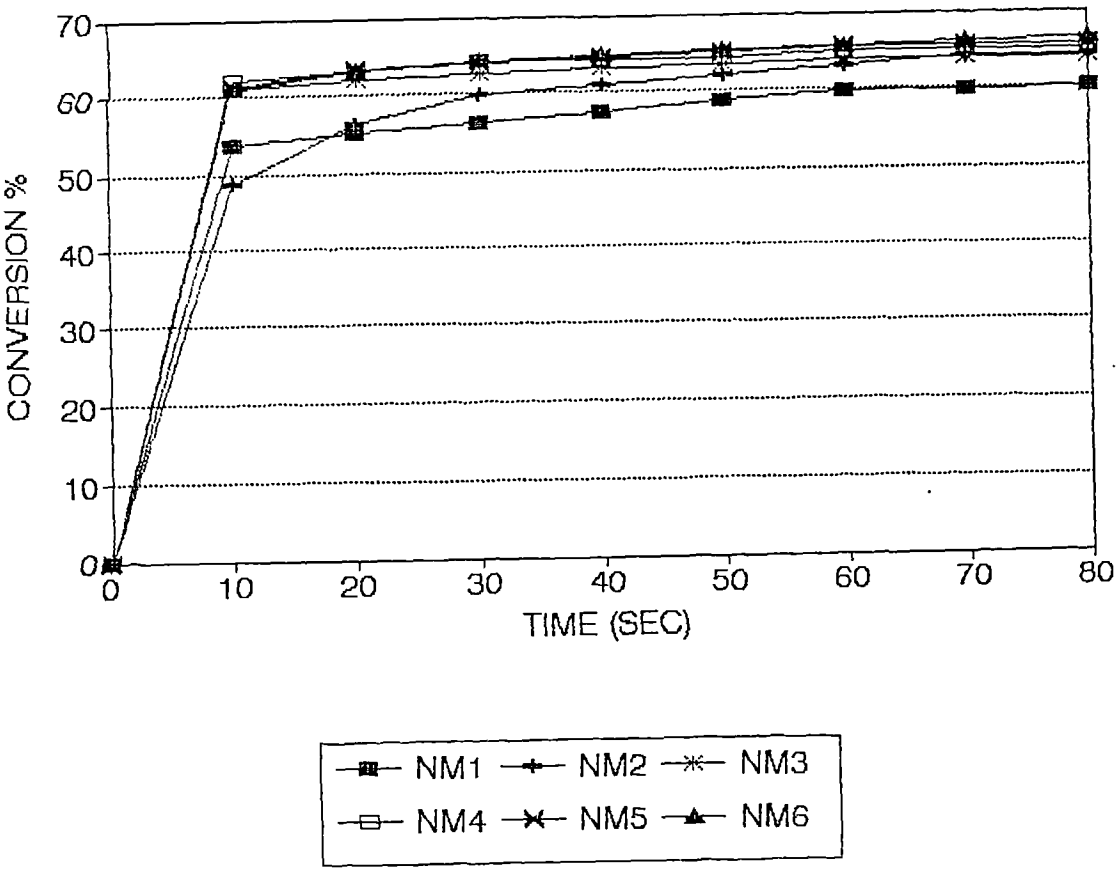


Fig 4.15 . Conversion % of samples (NM1-NM6) showing from RTIR during 80 sec of irradiation.

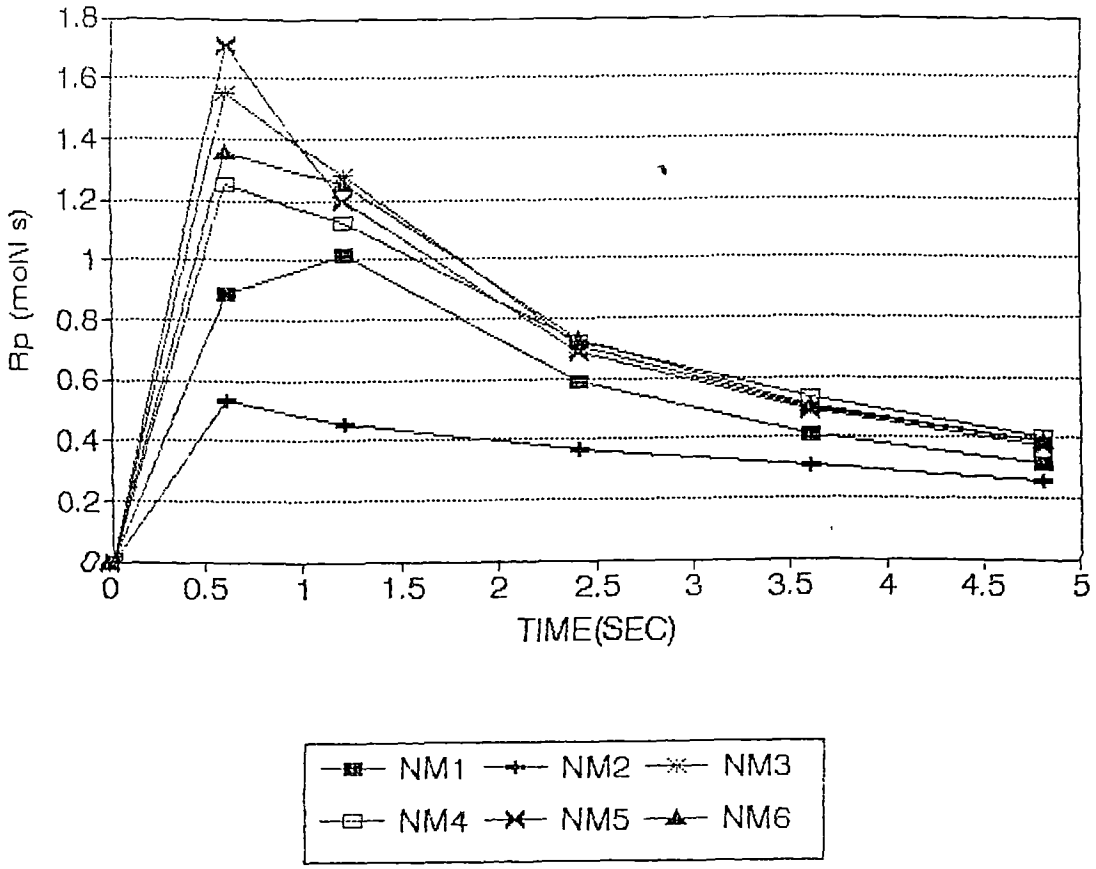
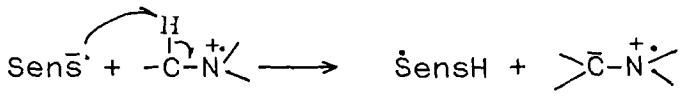


Fig 4.16. The rate of polymerisation of samples (NM1-NM6).

of the solvated radical ions, hydrogen transfer from the amine to the sensitiser occurs.



This process involves the transfer of a proton and therefore the acidity of the C-H bond should be of importance and this would dictate that the order of reactivity of alkyl groups attached to nitrogen is:

Primary>secondary>tertiary i.e. CH_3>-CH_2>-CH (20)

Although this trend has been generally observed, exceptions have been found [21-24].

N-methyldiethanolamine which is an excellent synergist helped to increase the efficiency of polymerisation in the case of Type II photoinitiators.

e) PHOTOYELLOWING

The yellowing of radiation cured systems may be attributed to many factors. The continued absorption by unused photoinitiator molecules of UV energy may induce reactions

deleterious to the film.

The initiator, the monomer and/or oligomer in the cured film and also the choice of amine synergist contribute to the yellowing of the samples.

The test method employed is based on an ASTM test procedure (E313-73) which is described in Chapter 9 for the measurement of indices of whiteness and yellowness of near-white, opaque materials. This procedure yields numbers that correlate to visual ratings of whiteness of standard white and near-white surfaces. The samples monitored in this study will be clear systems However, it is believed that the change in yellowness and the rate of yellowing would be relevant. The following variants were examined in this study:

a - varying photoinitiator type

b - varying monomer type

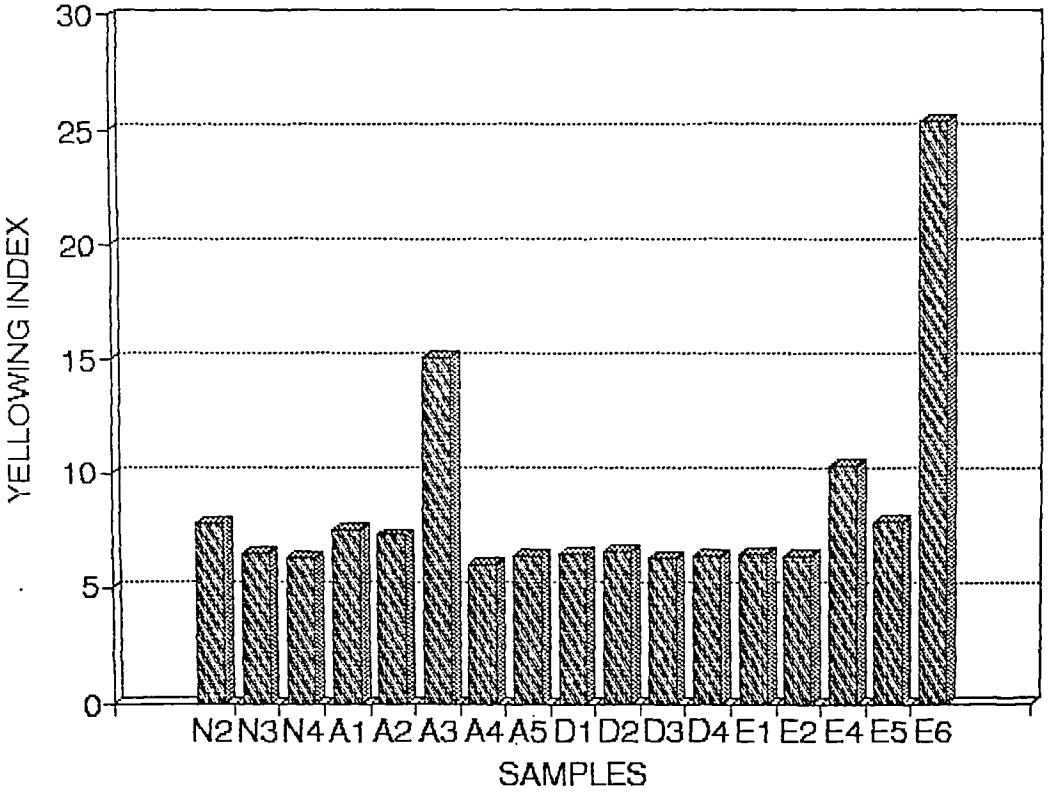


Fig 4.17 . Yellowing Indices of samples (N2-N4), (A1-A5), (D1-D4)and (E1-E6).

The samples are:

N1 = 5% Irg 907/P.3005/TPGDA /P.3005

N2 = 5% Irg 907/P.3005/CL.959 /P.3005

N3 = 5% Irg 907/P.3005/HDDA /P.3005

N4 = 5% Irg 907/P.3005/CL.960 /P.3005

A1 = 5% ITX/P.3005/CL.960 /P.3005

A2 = 5% BP/P.3005/CL.960 /P.3005

A3 = 5% Irg 369/P.3005/CL.960 /P.3005

A4 = 5% Irg 651/P.3005/CL.960 /P.3005

A5 = 5% Irg 907/P.3005/CL.960 /P.3005

IR1=D1 = 2% Irg 907/P.3005/CL.960 /P.3005

IR2=D2 = 3% Irg 907/P.3005/CL.960 /P.3005

IR3=D3 = 4% Irg 907/P.3005/CL.960 /P.3005

IR4=D4 = 5% Irg 907/P.3005/CL.960 /P.3005

NM1= E1 = 2% Irg 651/NMDEA/CL.960 /P.3005

NM2= E2 = 2% BP/NMDEA/CL.960

NM3= E3 = 2% CPTX/NMDEA/CL.960/P.3005

NM4= E4 = 2% ITX/NMDEA/CL.960 /P.3005

NM5= E5 = 2% Irg 907/NMDEA/CL.960 /P.3005

NM6= E6 = 2% Irg 369/NMDEA/CL.960 /P.3005

The co-initiator systems studied, which consisted of a hydrogen abstracting type of photoinitiator in combination with the tertiary amine, exhibited the greatest tendency

towards photoyellowing and have been previously shown [25], The benzoin- and benzil-based photoinitiator which both contain two aromatic moieties, were the second most susceptible group to photoinduced yellowing. Finally, the acetophenone-based photoinitiators produced coatings with the greatest resistance to photoyellowing.

The choice of photoinitiator obviously plays a major role in the photoyellowing of a UV-cured coating. In our study, Type I and Type II photoinitiators were used with the presence and absence of N-methyldiethanolamine. The yellowing indices results are shown in Fig.4.17.

Residual groups play a role in yellowing. The yellowing observed with Type I initiators is due to the terminal benzoyl and substituted benzoyl groups which are initiating polymerisation crosslinking and photooxidation via hydrogen abstraction. (In this case N-methyldiethanolamine seems to play a relatively small part) (Fig.4.17).

Except for A1, A2 and E2 and E4, all the samples belong to Type I group. The unexpected yellowing with A3 and E6 which contain Irg 369 and Irg 369 NMDEA respectively is probably due to substituents in the initiator e.g. the dimethylamino group (more detail given in Chapter 9).

Yellowing was observed with the Type II photoinitiators used in our study i.e. benzophenone and isopropylthioxanthone were used and yellowing is probably due to the reactions of unreduced aromatic ketone with N-methyldiethanolamine that caused the yellowing. A1 consisting of ITX and monomer gave less yellowing than E4 which contained N-methyldiethanolamine and substantiates our claim that amines promote yellowing which is in accord with the results of other workers [25,26,27,28].

VARYING MONOMER TYPE

Radiation-curing formulations prepared for coating applications usually consist of one or more acrylated oligomers or prepolymers and at least one multifunctional acrylate monomer. Gismondi has investigated several commercially available acrylate monomers for their resistance to UV-induced yellowing [28]. It was found that those containing an aromatic functionality or nitrogen were prone to photoyellowing, whereas binary mixtures of TEGDA and TMPTA were the most resistant to yellowing. Schmid found that aromatic urethane - and aromatic epoxy-based oligomers were more prone to photoyellowing than their aliphatic analogues [29]. The photoyellowing associated with aromatic-based oligomers is believed to be due to the

formation of quinoid structures. Allen and McKellar have demonstrated that aromatic urethanes based on MDI oxidised to a highly coloured quinone-imide product [30]. Decker and Bendaikha have studied the photodegradation of UV-cured epoxy acrylate networks using IR and O_2 uptake measurements [31] CL-959 oxazolidone monoacrylate, CL-960 carbamate monoacrylate and 1,6 hexanediol diacrylate were tested with 5% photoinitiator Irg-907. The results are given in Fig.4.17. The samples N2, N3 and N4 represented initiator/ CL-959, I/HDDA and I/CL-960 in photomer 3005 acrylated epoxy. According to our results CL-959 gave the highest yellowing index compared to diacrylate HDDA and monoacrylate CL-960.

PENDULUM HARDNESS

The hardness of a coating is dependent upon the functionality and chemical structure of the prepolymer used, as described previously in Chapter 1 . The pendulum hardness provides information about the degree of conversion since it is directly related to the crosslink density of the cured coating [32,33].

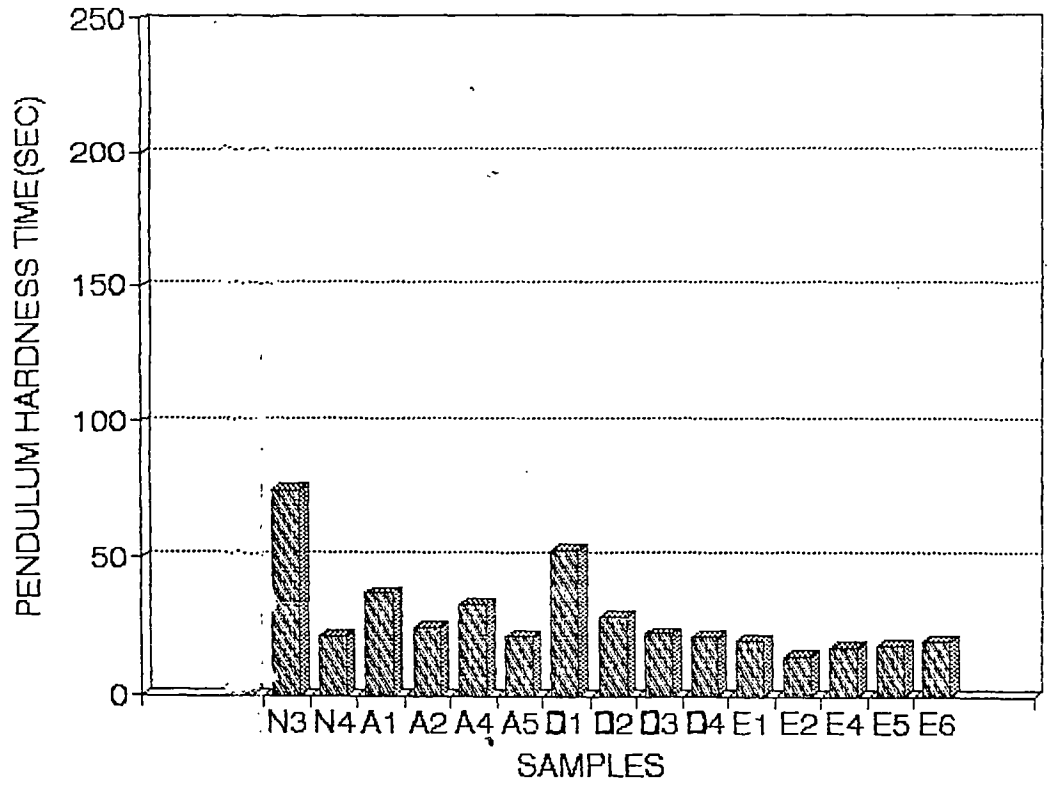


Fig 4.18. Pendulum Hardness Results of (N3-N4), (A1-A5),(D1-D4) and (E1-E6).

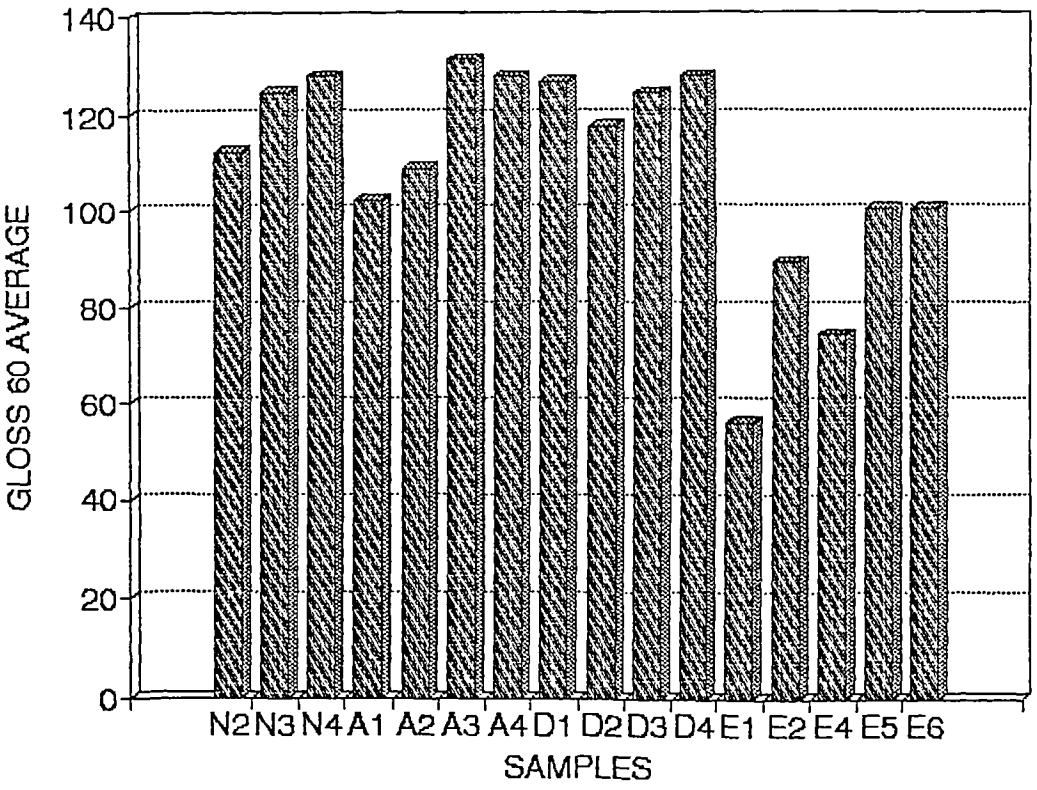


Fig 4.19. Gloss 60 Average Results of (N2-N4),(A1-A5),(D1-D4) and (E1-E6).

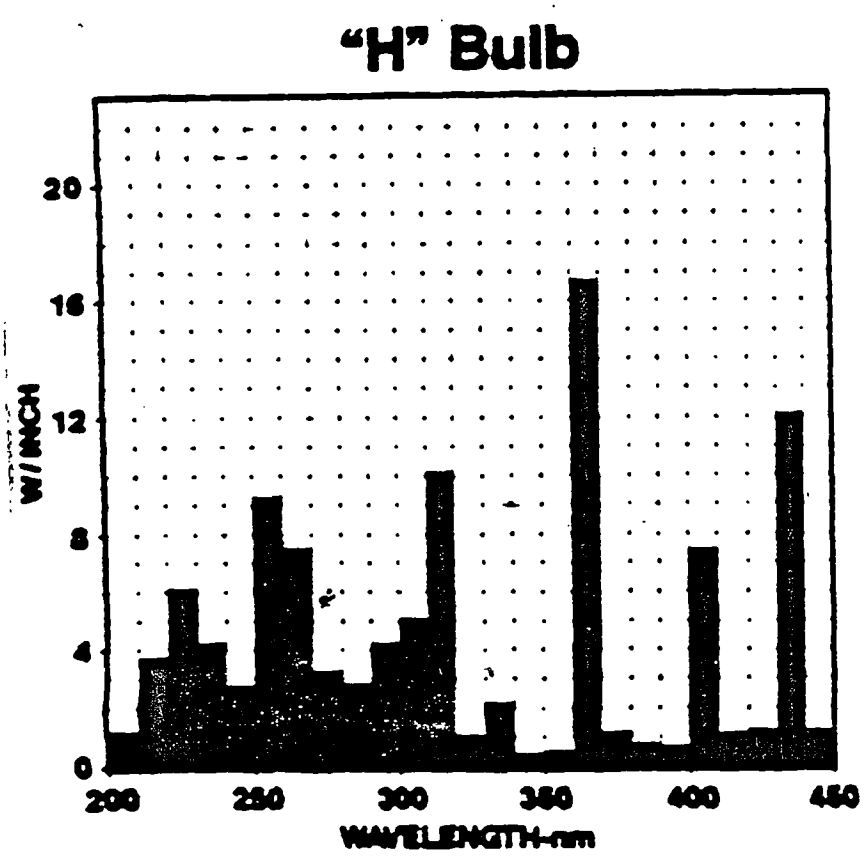


Fig 4.20. The spectral output of "H" Bulb.

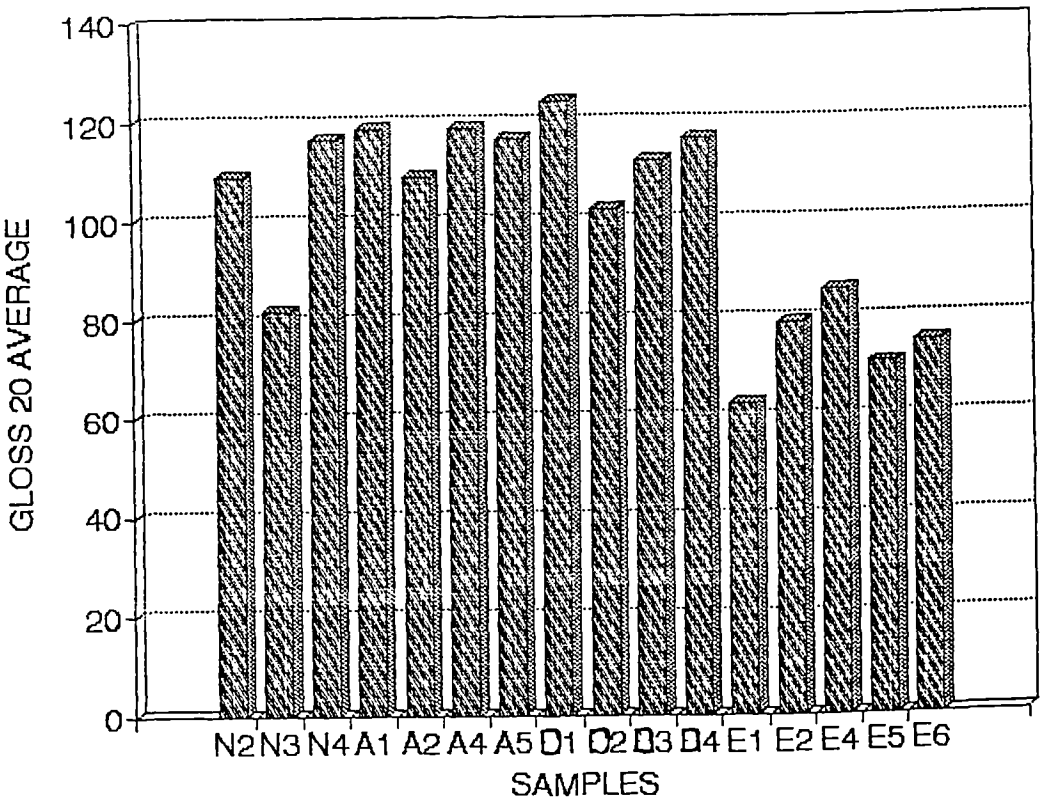


Fig 4.21 Gloss 20 Average Results of (N2-N4), (A1-A5),(D1-D5) and (E1-E6).

The ability of the cured coating to resist abrasion is an indication of the toughness of the film. The harder the cure, i.e. the greater the crosslinked density, the greater the resistance to abrasion [34].

The dampening of the pendulum oscillations were recorded in seconds for all formulations. All samples were cured using a standard "H" bulb, (Fig 4.20) at 300w per inch output. The pendulum dampening results are given in Fig 4.18. The samples were given in one pass where the speed of the belt was 5 metres per minute.

The photoinitiating efficiency of these photoinitiators which were presented in Chapter 5 using RTlR spectroscopy were tested on an abraded aluminium panel using König Pendulum Hardness test [6]. Pendulum hardness is related primarily to the cure response and the crosslinked density of the coating [38]. Infrared techniques have also established a good correlation between the pendulum hardness and the residual unsaturation within the film [6]. Therefore, the pendulum hardness values can be used as an approximate parameter for determining the degree of cure within a film. All pendulum hardness values were determined for a 24μ film on the abraded aluminium panel. The results in Fig 4.18 show that changing the initiator and changing the initiator concentration caused differences in the cure speeds. 2% Irg 907 provided a much higher hardness value compared to

3, 4 and 5% Irg 907 samples. All initiators in the presence of NMDEA in the formulation always lead to a decrease in the pendulum hardness. This is possibly due to the fact that at higher amine concentrations the plasticising effect of amines or their ability to act as chain transfer agents [6], leads to the formation of lower molecular weight polymers and a consequent reduction in the apparent degree of cure.

GLOSS

Gloss measurements were recorded using 20^{o} head and 60^{o} head of glossmeter. It is generally accepted that gloss is a sensitive indicator to film degradation; often showing significant variation long before chemical change can be detected.

But gloss is not a reliable indicator for durability. There are some important factors which affect gloss levels e.g. photoinitiators, UV intensity etc. The best gloss is obtained with low intensity radiation.

Gloss level results are shown in Figs 4.19 & 4.21 respectively for 20^{o} and 60^{o}. High gloss levels indicate good quality films.

The formulations with amine produced lowest gloss level for either 20^{o} or 60^{o} (Figs.4.19 & 4.21). This is possibly due to oxidation products. As can be seen easily from Fig.4.19 and Fig.4.21 diacrylates have lower gloss levels than monoacrylate, possibly due to a shrinkage problem, which leads to a lower gloss.

RTIR studies using a mixture of a monoacrylate (C1-960) and an epoxy for acrylate (P3005) show that simple aromatic ketones such as benzophenone and thioxanthone are inefficient initiators in the absence of an amine. The reactivity of the Type I initiators Irg-651, 907 and 369 reflects their UV absorption spectra (Fig. 4.2) with Irgacure 369 exhibiting the greatest reactivity (N.B. all initiators were used in a weight/ weight basis). Similar results were obtained when tripropyleneglycol diacrylate (Figs. 4.3 and 4.5) (TPGDA) was used as the polymerisable monomer. The Type II initiators, benzophenone, chlorothioxanthone and isopropylthioxanthone show limited reactivity. The Type I photoinitiators Irg-651 and Irg-907 show relatively high reactivity with the better absorber Irg-907 showing the greatest reactivity. That CL-960 is a highly reactive monoacrylate is shown by the results displayed in Fig. 4.4 where it can be seen that Irgacure 369 and 907 effect rapid cure in a short time a >60% of the acrylate double bond are consumed. Irgacure 651, because of its poorer absorbance properties is less reactive. Although the performance of ITX is not wonderful, it does lead to 30% conversion of the acrylate double bonds and this suggests that the monoacrylate possesses some reactive C-H bonds. Benzophenone, as in all the other systems stretched was the least reactive.

Figs.4.8-4.10 display the effect of varying photoinitiator concentration By varying the weight of initiator used from 2 to 5% a small change in rate is observed. It would appear that when Irgacure 907 is used at 5% w/w, all the light is not being absorbed and that this concentration is not changing the viscosity of the mix too much. From a practical point of view there seems to be little value in using Irgacure at a level >2%.

The performance of a photoinitiator is strongly affected by the nature of the polymerisable monomer. This can be seen from Figs. 4.11 and 4.12. Interestingly the diacrylates HDDA and TPGDA are less reactive than the monoacrylates CL 959 and 960. This may be due to the viscosity increasing with cure more rapidly for the diacrylates than for the monoacrylates.

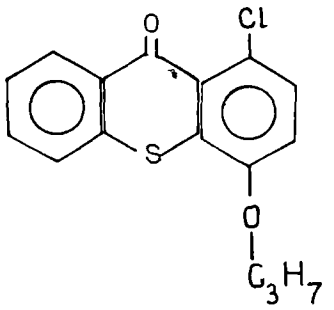
When amines (in this case N-methyldiethanolamine) are included in the formulation, the Type II initators perform well (Figs. 4.14 and 4.15). Benzophenone, which without amines performs poorly, gives after a reasonable irradiation period, 60% conversion of the acrylate double bonds. Both isopropyl, thioxanthone and chlorothioxanthone are highly efficient and this in part reflects the fact that they absorb so well in the range 300-400nm.

The efficiency of cure by Irg-907 and 369 does not look all that different to what is observed in the absence of amine (Fig. 4.2). Since in RTIR experiments oxygen quenching is not important, the only role for the amine is to cause some of the initiator to react by being reduced by the amine. In these experiments this does not appear to be a major route.

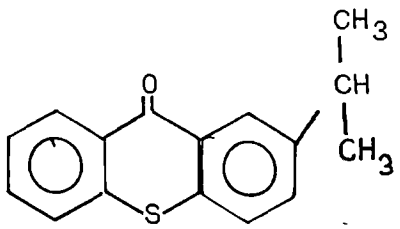
EXPERIMENTAL

Materials: The photopolymerisable resins used in this work contained three main components:

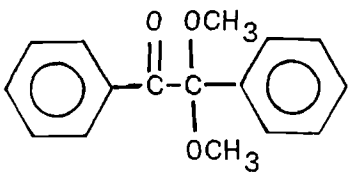
(i) Photoinitiators: benzophenone, 1-chloro-4-propoxy thioxanthone from International Bio Synthetics,



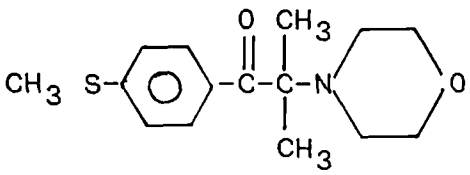
Isopropylthioxanthone (mixture of 2 and 4 isomers)



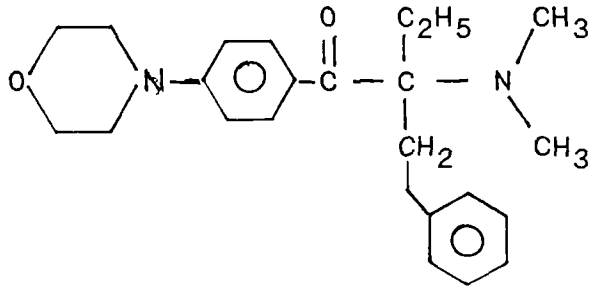
2,2-Dimethoxy-2-phenylacetophenone Irg-651



2-Methyl-1-[4-(methylthio)phenyl]-2-morpholino propane-1-one



2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl-butan-1-one

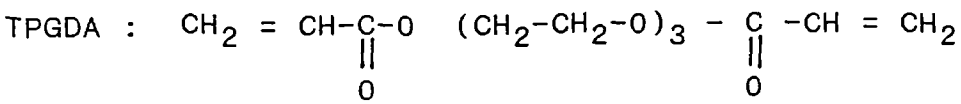


from Ciba-Geigy

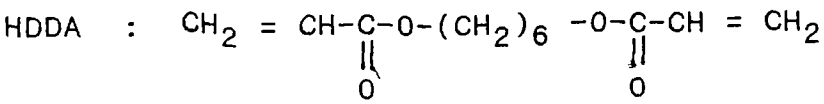
(ii) Acrylated epoxidised oil photomer 3005 was chosen.

(iii) A reactive acrylic diluent, tripropylene glycoldiacrylate (TPGDA from UCB), hexanedioldiacrylate (HDDA from SNPE) oxazolidone monoacrylate (Acticryl CL-959 from SNPE), carbamade monoacrylate (Acticryl CL-960 from SNPE) with the following formula:

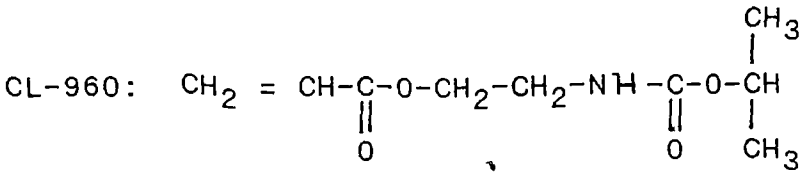
TPGDA :



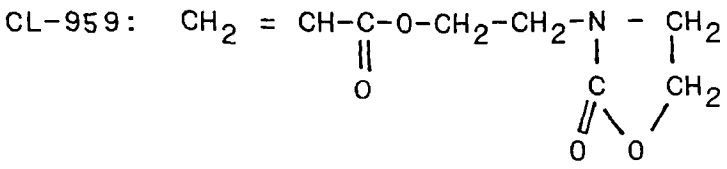
HDDA :



CL-960:



CL-959:



and N-methyldiethanolamine was used as a synergist from Aldrich.

Typical formulations contained 5% of photoinitiator and equal parts of the acrylic oligomer and diluent. The resin was applied on an NaCl salt disc as a uniform layer of thickness 24μ. The coated disc was placed into an infrared spectrophotomer, the spectrum was taken before and after UV exposure, and the IR wavelength was fixed at 810 cm^{-1} where the acrylic double bond exhibits a sharp and distinct absorption. The detection of the IR signal was made by operating the spectrophotometer in the transmission mode.

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CHAPTER 5

SENSITISATION OF IRG-907 BY ITX

Chapter 5. SENSITISATION OF IRG-907 BY ITX

SENSITISATION OF IRG 907 BY ITX

INTRODUCTION

During the last decade, UV-curing has developed from a technological innovation to a widely-used procedure for coating and printing surfaces. In this period, prepolymers, reactive diluents, additives such as pigments or stabilisers as well as photoinitiators have been constantly improved and supplemented with new products.

The prepolymers employed have shown the greatest influence on the final properties of the cured coating. Both the start and the course of the polymerisation reaction, however, depend on the photoinitiator system (PI) used.

A major improvement in this field was made with the introduction of substituted α-aminoketo photoinitiators [1,2]. These compounds have higher absorption coefficients in the 300-400nm region than the usual acetophenone type photoinitiators and are, therefore suitable for the curing of pigmented systems.

The reactivity of these systems is further improved by the addition of sensitisers such as thioxanthones [1-3]. This enhancement of reactivity is due to the fact that thioxanthones have longer wavelength absorptions (λ_{max} =

380nm) than acetophenone type photoinitiators and consequently are of value for use with pigmented systems. This allows better utilisation of the light passing through the spectral window of the pigment. The photoinitiator is subsequently activated by interaction with the excited state sensitiser. The observation that α-cleavage of Irg 907 is sensitised by thioxanthones raises the question as to whether it is a triplet-triplet energy process or involves energy from the thioxanthone passing directly into the C-C bond which rapidly undergoes cleavage.

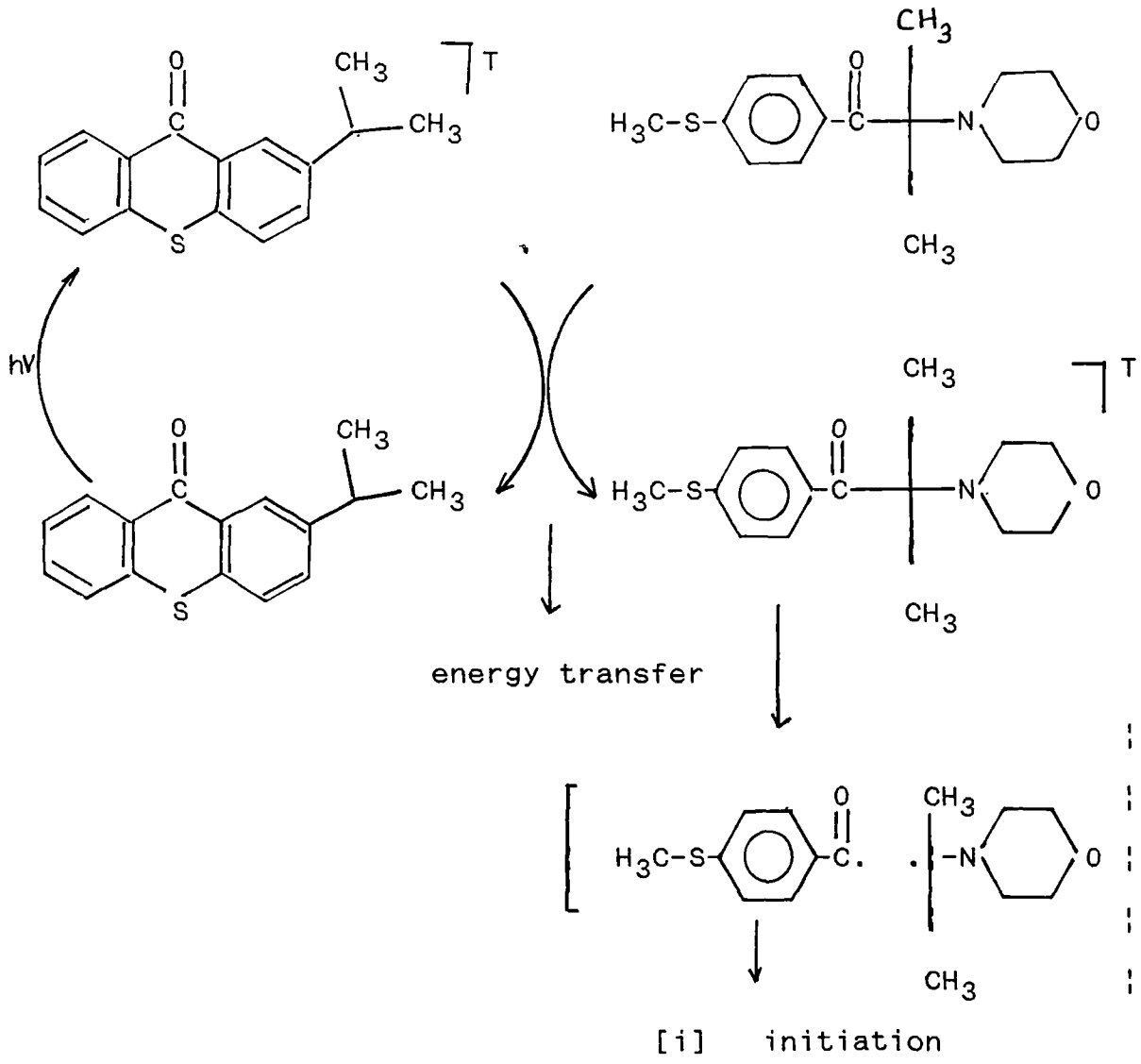
Triplet energies of α-aminoketones, substituted on the benzoyl moiety with thiomethyl or amino groups, are in the range of 61-63 kcal/mol and are hence significantly lower than those of other acetophenone photoinitiators [4].

Thioxanthones have triplet energies situated around 59-63 kcal/mol and cannot sensitise the decomposition of benzil dimethylketal (E_T=66.2 kcal/mol) for example, by an energy transfer process since this would be an endergonic process. However, energy transfer is possible for certain sensitiser/ α-amino ketone derivatives, where:

$$E_T \text{ (sensitiser)} > E_T \text{ (initiator)}$$

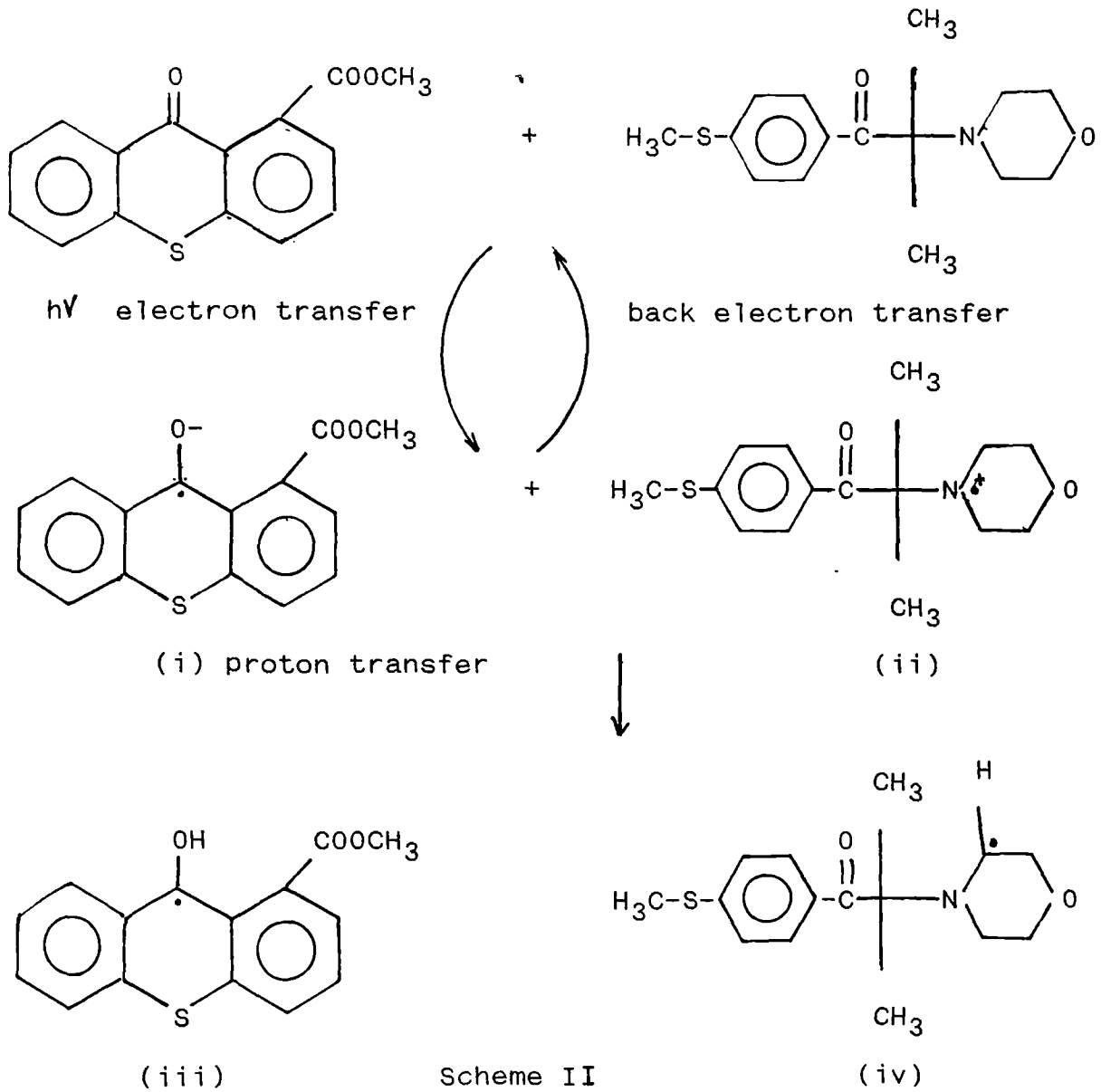
The triplet energies of isopropylthioxanthone, 2-methyl-2-carbethoxythioxanthone and Irg 907 are 61.4 kcal/mol^{-1}, 58.4 kcal/mol^{-4} and 61 kcal/mol^{-1} respectively, which probably

means that the energy transfer process is isoenergetic or even slightly endothermic [5]. Therefore, it is difficult to accept that the sensitisation is an energy transfer process as shown in Scheme I by Fouassier [6].



Scheme I Energy-transfer induced α-cleavage of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one Irg 907

These results were backed up by the findings that Irg 907 quenches the triplet state of thioxanthones with rate constant of 2.4 x 10^8 $m^{-1}s^{-1}$ and 6.3 x 10^8 $m^{-1}s^{-1}$ in toluene and methanol respectively [5]. The ClDNP experiments also indicate that electron transfer between the morpholino group of Irg 907 and triplet 2-carbomethoxythioxanthone occurs. It is not known to what extent this reaction contributes to the initiation process (SchemeII).

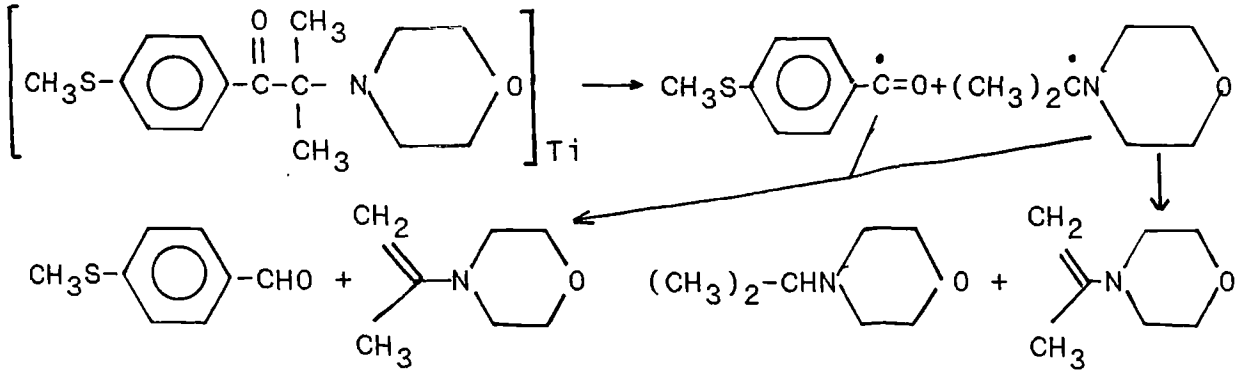


Scheme II

The interactions between thioxanthones and Irg 907 have been the subject of laser flash photolysis studies [7,8,9].

In the early work it was claimed that in non-polar solvents the sensitisation process is via energy transfer and in polar solvents via electron transfer with the morpholino group acting as an electron donor [7]. This seems surprising in view of the poor quenching ability of N-methylmorpholine which is a particularly hindered morpholine. Our recent experiments [10] showed that N-isopropylmorpholine acts as a physical quencher of many triplet states and is a most inefficient hydrogen donor (as mentioned in Chapter 6). This would suggest that the electron transfer process makes little positive contribution [1].

Recent CIDNP experiments have shown unequivocally that thioxanthones do sensitise the α-cleavage reaction of Irg 907 [3,11] Scheme III.



Scheme III

RESULTS AND DISCUSSION

The initiation efficiency of α-aminoketones which undergo α-cleavage [2,3] was found to be increased by sensitisation using isopropylthioxanthone as a triplet sensitiser. Isopropylthioxanthone is a well known Type II photoinitiator and it is very efficient when tertiary amines are used as a synergist in such curing systems. Tertiary alkyl amines [12] aromatic amines [13] and functionalised amines [14] have recently been reported to be effective in accelerating the photopolymerisation of an air saturated diacrylate formulation. The degree by which the rate of polymerisation increases is dependent upon the structure of the amine, as well as its concentration. As amines act both as oxygen scavengers and chain transfer agents [15], the amine concentration required to maximise the photopolymerisation rate is critical. The main problems encountered when simple aromatic and aliphatic amines are employed as oxygen scavengers are the chain transfer and/or inhibition step which involves the transfer of the polymer radical to the amine by a standard hydrogen abstraction mechanism. If the amine concentration is large, the hydrogen abstraction process dominates and the kinetic chain length of the average growing polymer chain decreases, If, in addition the re-initiation process is slower than the chain propagation process, the polymerisation rate decreases further.

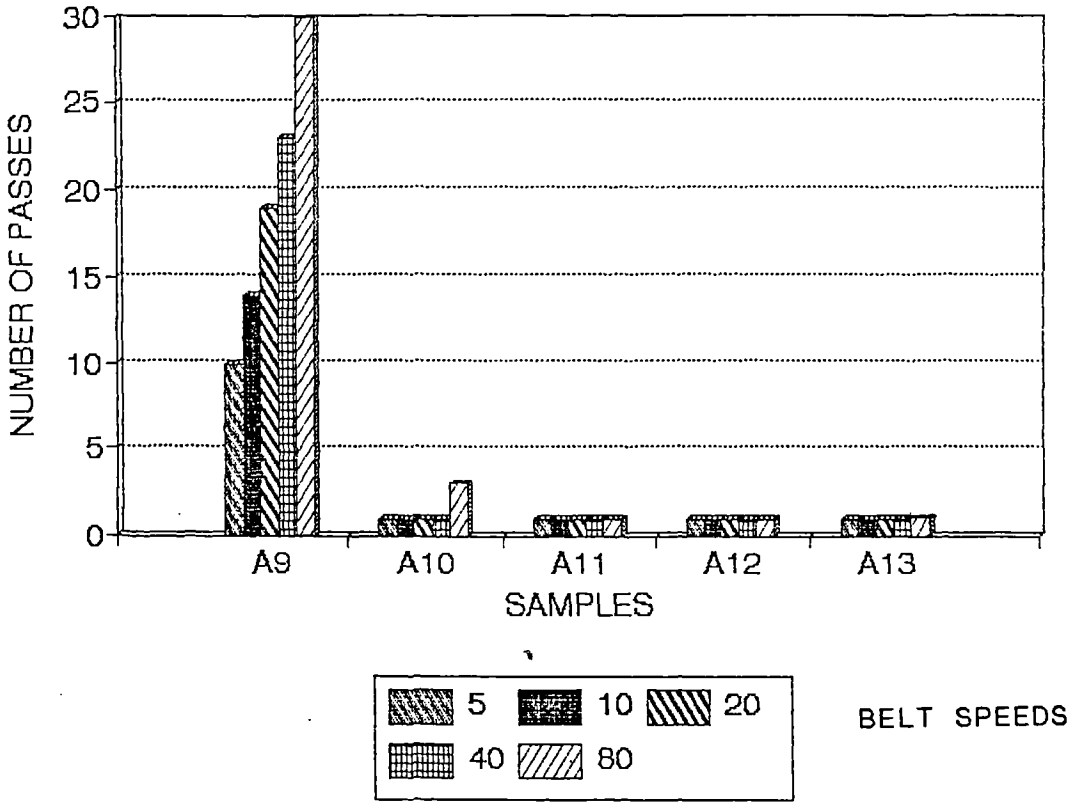


Fig 5.1. The curing results of samples (A9-A13) in air .

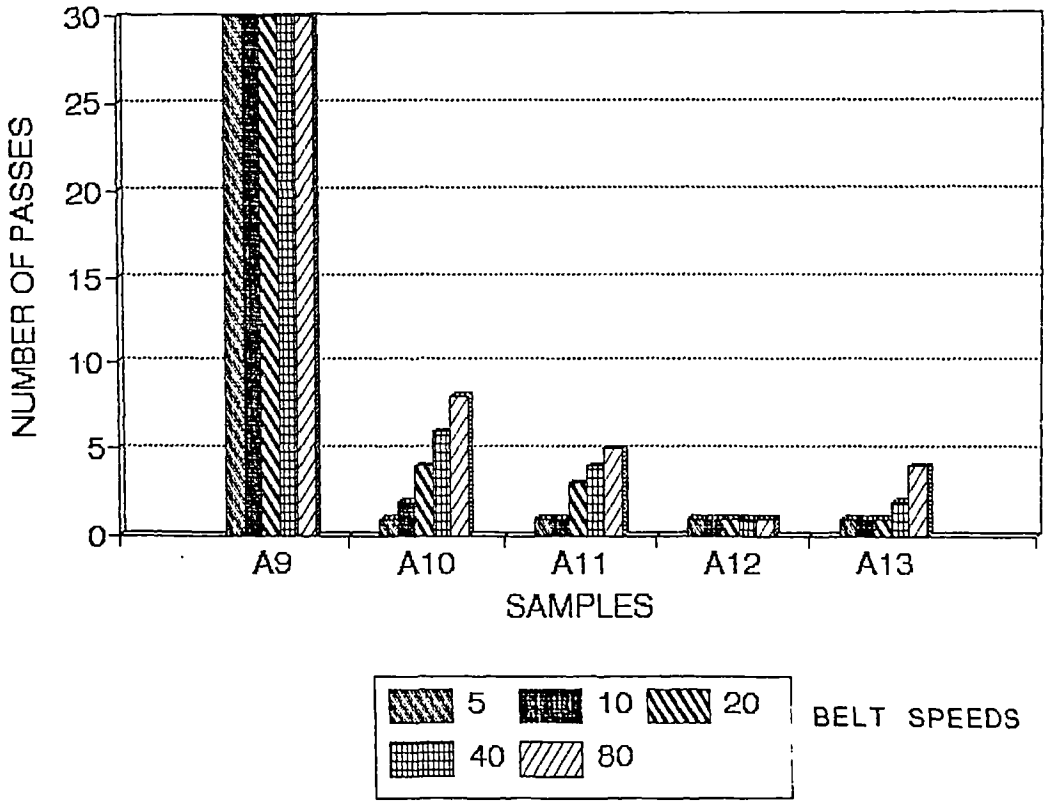


Fig 5.2. The curing results of samples (A9-A13) using a glass filter.

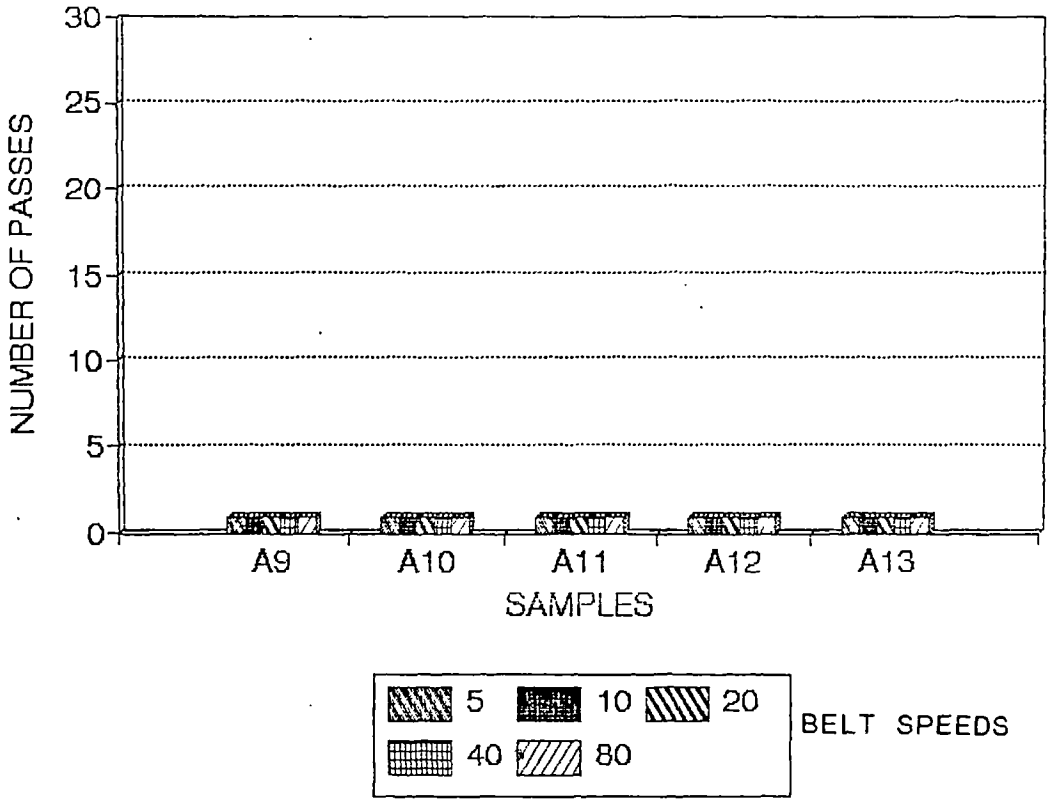


Fig 5.3. The curing results of samples (A9-A13) using a glass coverslip.

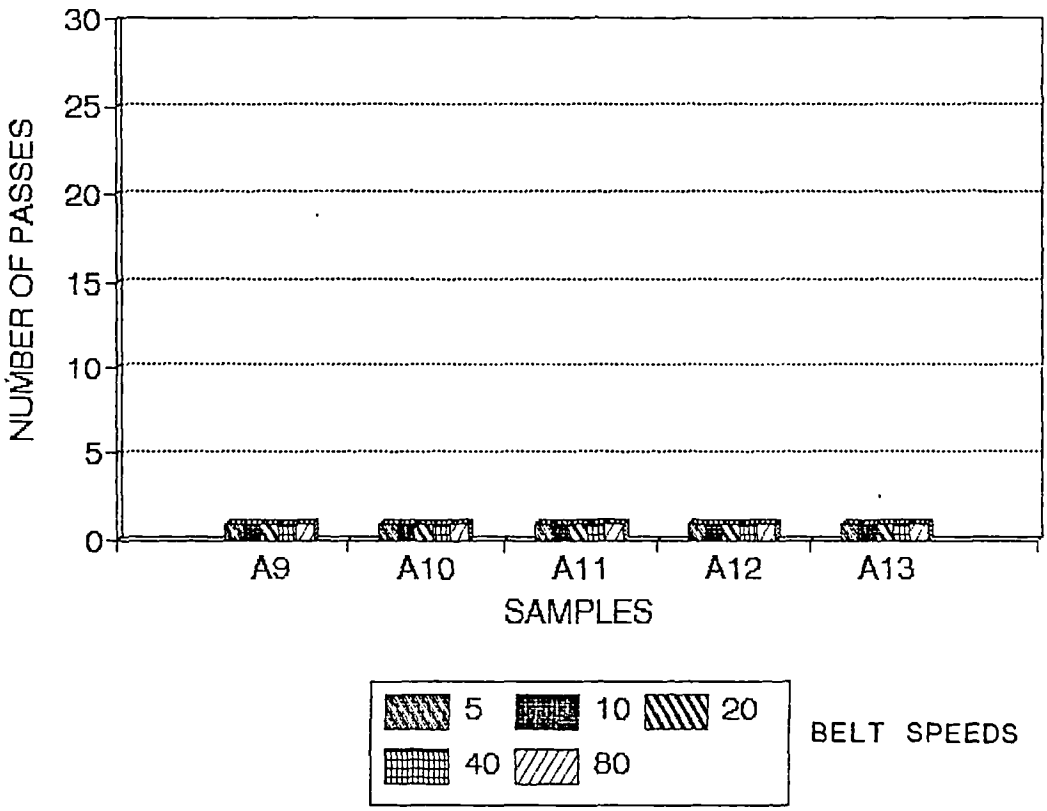


Fig 5.4. The curing results of samples (A9-A13) using a quartz coverslip.

An investigation varying the amine concentration was carried out using Irg-907 and ITX as initiators and NMDEA at the 10 and 30% level using a 100W per inch medium pressure mercury lamp for curing in air, through a glass filter and glass and quartz coverslip. From this set of experiments the effect of O_2 inhibition and restricting irradiation wavelengths greater than 300nm could be investigated. The results were compared with each other and with a blank sample of Irg-907.

The results were obtained for different belt speeds with the number of passes to achieve tack-free results being recorded. If no cure was observed after 30 passes the system was classed as being poor.

The samples were irradiated under a quartz and glass coverslip through a glass filter and by direct irradiation. From this set of experiments the effect of O_2 inhibition and restricting irradiation wavelengths greater than 300nm could be investigated.

A9: 2% Irg 907
TMPTA

A10: 2% Irg 907
10% NMDEA
TMPTA

A11: 2% Irg 907
30% NMDEA
TMPTA

A12: 2% ITX
10% NMDEA
TMPTA

A13: 2% ITX
30% NMDEA
TMPTA

The results are shown in Figs.5.1, 2, 3 and 4 respectively and were obtained cured in air, with glass filter, glass coverslip and quartz coverslip.

According to UV-curing test results the effect of amine on Irg-907 - TMPTA system is very positive as shown in Fig.5.1 (cf. A9 with A10)

This advantageous effect can be attributed to the known ability of amines to act as efficient oxygen scavengers [12-14,15,16,17,18], thus counteracting the oxygen inhibition of the chain propagation reaction. Irg 907 on the other hand a photoinitiator which undergoes a Norrish Type I photocleavage producing radicals which possess initiating properties [15,19]. This photoinitiator generates radicals by an extremely fast photocleavage mechanism [3] and it is therefore very unlikely that the initiator should need added synergist, such as tertiary amines to produce initiating free radicals. Thus the beneficial effect of amine under these experimental conditions is most probably that of an efficient oxygen scavenger. This was proved by using a glass coverslip and quartz coverslip on the film. The results are shown in Figs. 5.3 and 4; Photo-DSC results also confirmed the same results. It is easy to see the reduction process of Irg 907 as shown in Figs 5.5 and 6,under nitrogen while N-methyldiethanolamine was especially favouring .

Photoinitiators, such as benzophenone and thioxanthones were used in conjunction with tertiary amines [20] because they generate free radicals by a hydrogen abstraction mechanism upon irradiation of UV light [15,18,21,22]. The excited carbonyl group abstracts hydrogen from the amine to give an α-aminoalkyl radical, which is responsible for initiating polymerisation [15,18,23]. All test results are shown in

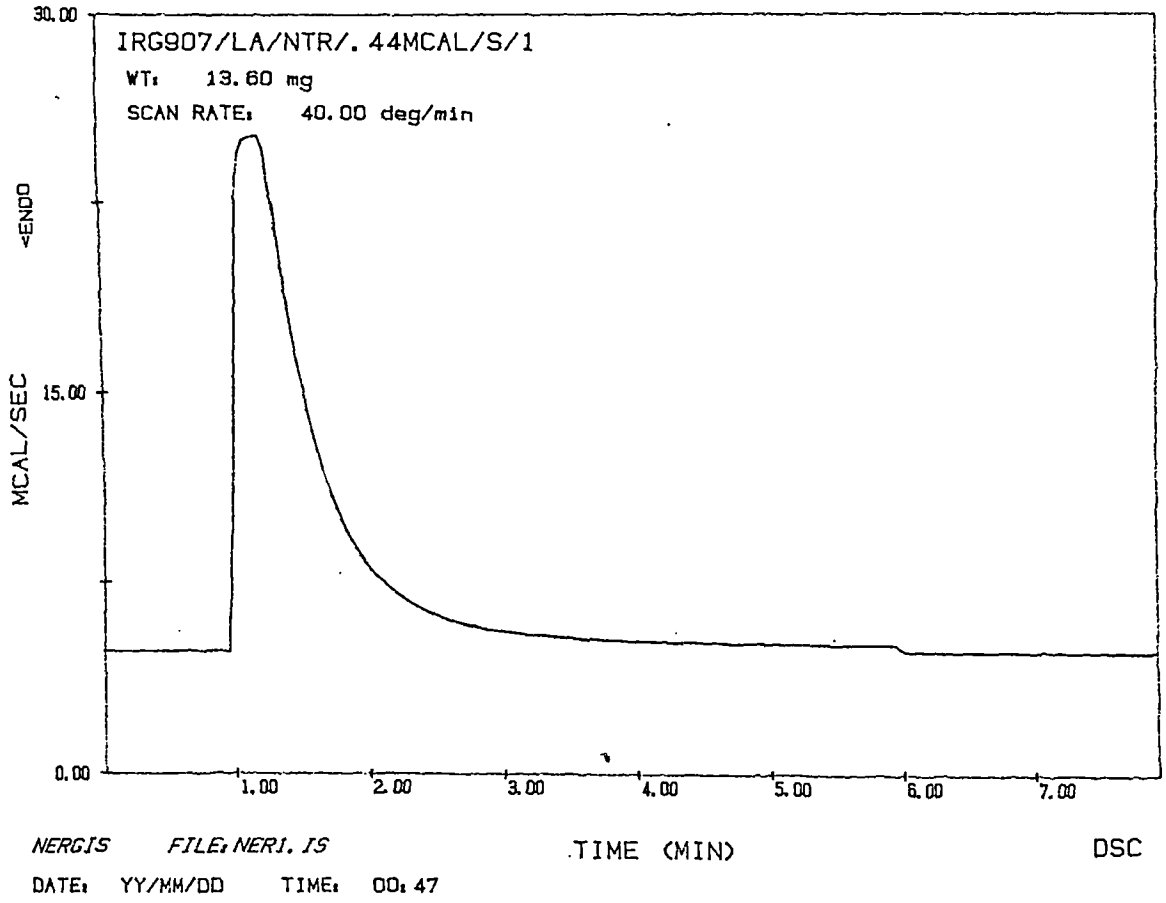


Fig 5.5. DSC trace for photopolymerisation of 2% IRG-907/LA in nitrogen.

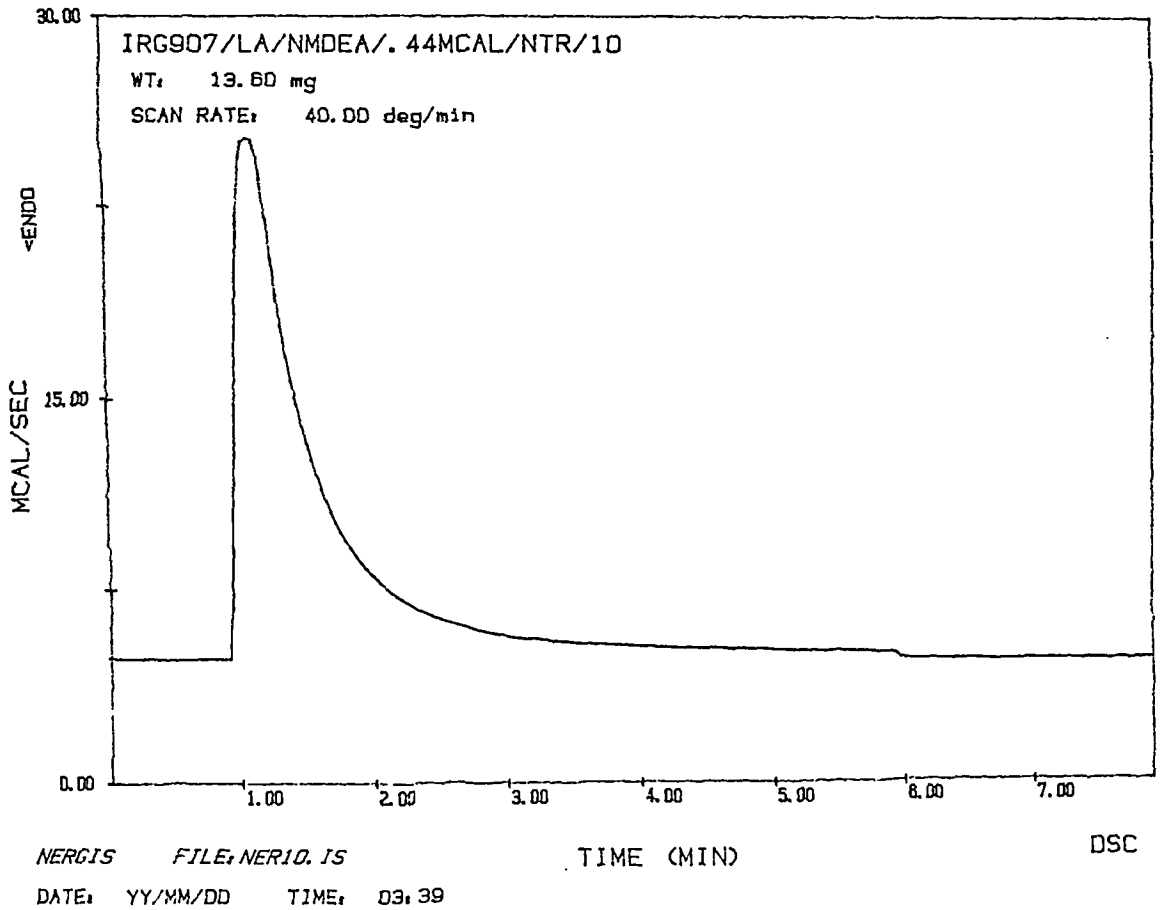


Fig 5.6 DSC trace for photopolymerisation of 2% IRG-907/10% NMDEA/LA in nitrogen.

Figs 5.1, 2, 3 and 4 ,for different amine concentrations.

From the results obtained for ITX, it would appear that at higher amine concentrations the plasticising effect of amines or their ability to act as chain transfer agents [15], leads to the formation of some lower molecular weight polymers and a consequent reduction in the apparent degree of cure (Fig 5.1 and 5.2).

The optimal photoinitiator and tertiary amine concentrations are very important for curing. That an optimal concentration of photoinitiator exists in free radical polymerisations has been reported [12,13] and attributed to screening (inner filter effects at higher photoinitiator concentrations) thereby preventing a complete through cure. This effect was found to be very marked for film thickness greater than 1mm [12-16].

Curing systems containing photoinitiator (Irg 907) and photosensitiser (ITX) were prepared. The effect of varying the sensitiser should make it easier to judge the contribution of ITX to the system's efficiency. The synergist effect of amines on Type II photoinitiators (ITX and BP) was investigated. Two different amines were used, namely (N-methyldiethanolamine (NMDEA) and triethylamine (TEA). All the reactions were performed using trimethylolpropane triacrylate. The results of these investigations are clearly shown in Fig. 7 for cure in air. All the other results are

shown in Figs 5.8,9 and 10 respectively, for glass filter, and glass coverslip and quartz coverslip.

The formulations are:

B1 : 2% Irg 907
1% ITX
10% NMDEA
TMPTA

B2 : 0.5% Irg 907
10% NMDEA
TMPTA

B3 :0.5% Irg 907
0.25% ITX
10% NMDEA
TMPTA

B4 :0.25% BP
10% Et_3N
TMPTA

B5 :0.25% BP
10% NMDEA
TMPTA

B6 :0.25% ITX
10% Et_3N
TMPTA

B7 :0.25% ITX
10% NMDEA
TMPTA

B8 :0.25% Irg 907
TMPTA

B9 :0.25% ITX
0.25% Irg 907
TMPTA

B10 :0.75% Irg 907
TMPTA

B11 :0.75% Irg 907	B12 :0.25% Irg 907
0.5% ITX	0.5% ITX
TMPTA	TMPTA

Comparison of the results for B1 and B3 shows that reducing the percentage of initiator + sensitiser in the mixture from 3% total to 0.75% total has little effect (the differences only becoming apparent at the higher belt speeds). When the performance of B2 with B3 is compared it can be seen that the addition of ITX improves the rate of cure.

Comparison of B8 with B9, and B10 with B11, and B9 with B12 also shows that addition of ITX increases the rate of cure. The results depicted in the Figure clearly show that NMDEA is a far better synergist in Type II initiator systems than triethylamine (when B4 is compared with B5 and B6 with B7). This point is expanded upon in Chapter 8 . When a glass filter is interposed between the light source and the film it appears beneficial to increase the initiator concentration (of B1 with B3) and this is presumably due to the requirement for improving the efficiency of light capture. When the effect of oxygen is removed, curing is so efficient that all the systems behave similarly irrespective of whether a glass or quartz filter is used.

Finally, oxygen inhibition was investigated by using a quartz coverslip and glass coverslip. The results in Fig.5.3 and

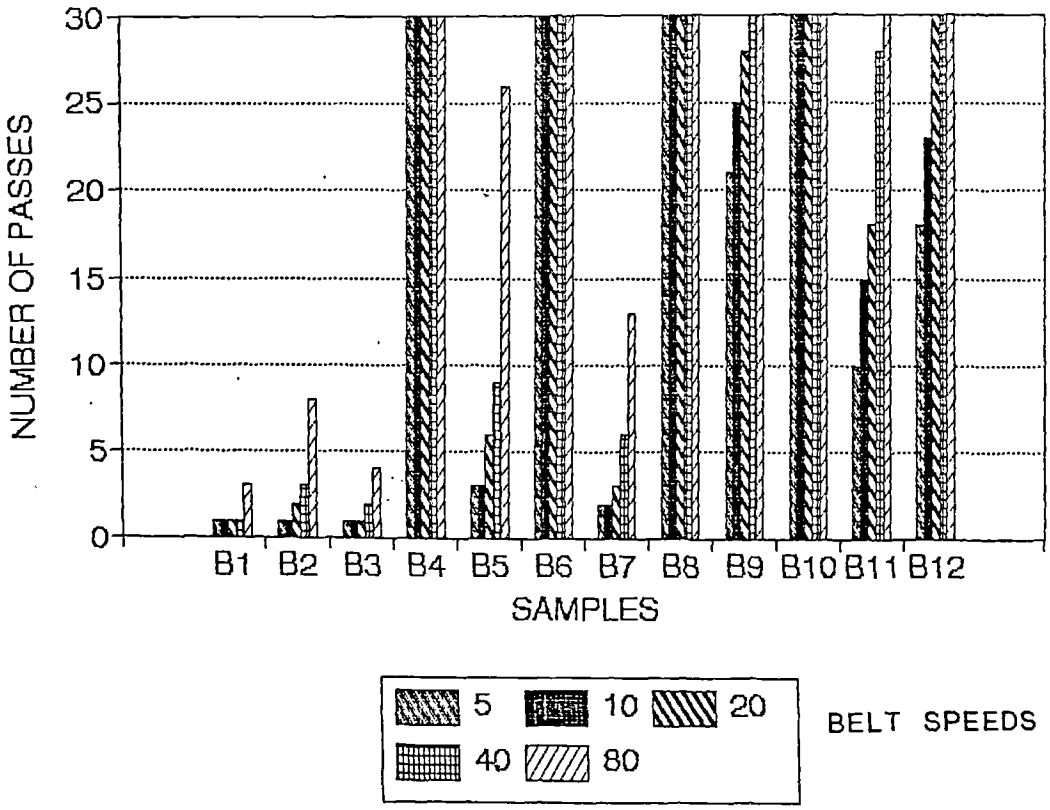
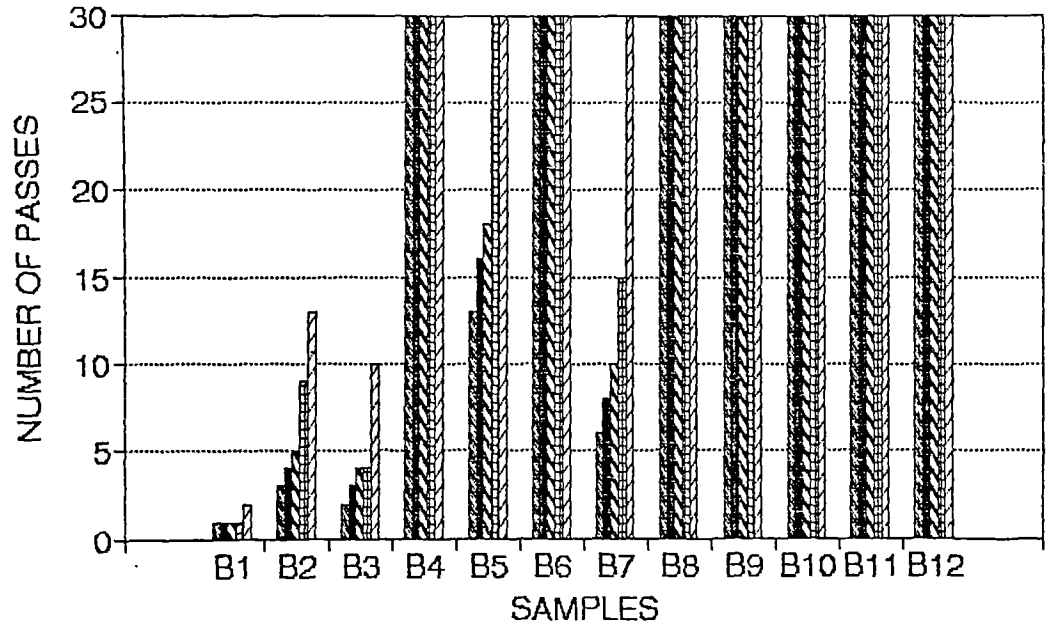


Fig 5.7. The curing results of samples (B1-B12) in air.



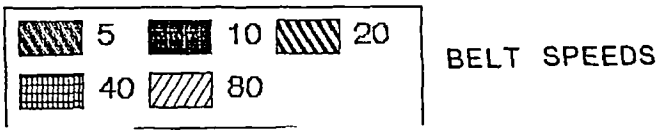


Fig 5.8. The curing results of samples (B1-B12) using a glass filter.

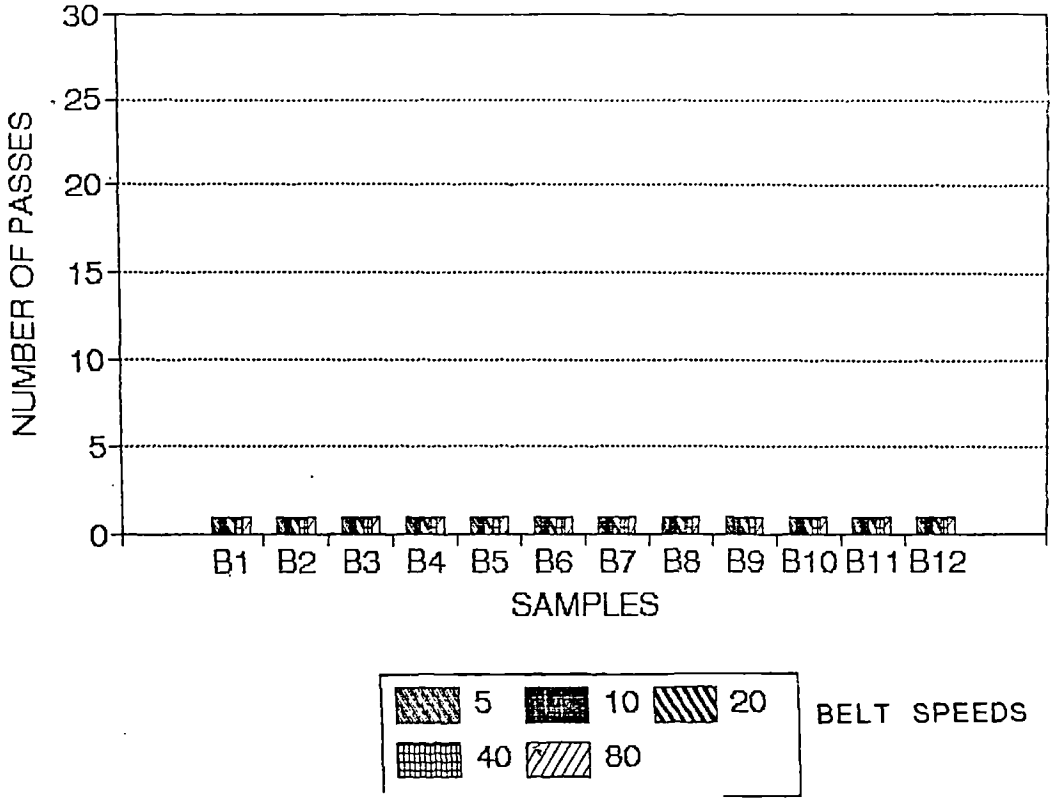


Fig 5.9 The curing results of samples (B1-B12) using a glass coverslip.

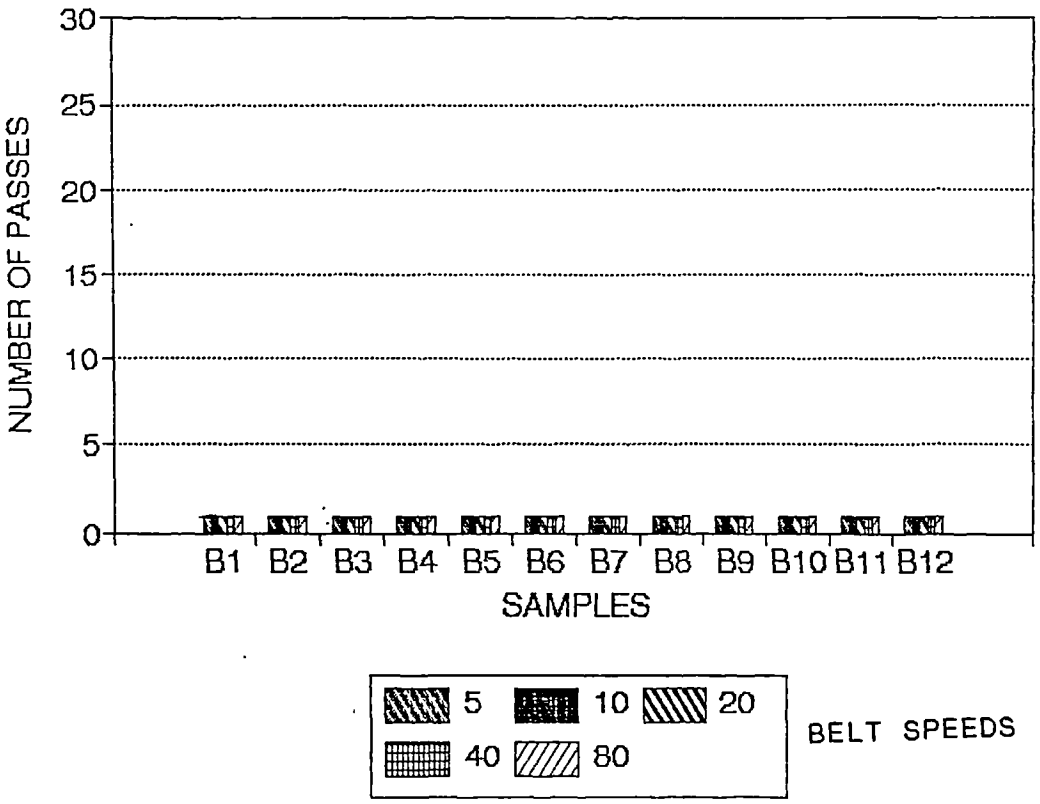


Fig 5.10 The curing results of samples (B1-B12) using a quartz coverslip.

Fig.5.10 show how dramatically the presence of oxygen affects the performance of the photoinitiator. In the absence of oxygen all the samples were able to effect cure without an amine synergist.

In conclusion, ITX was shown to sensitise the Type I fragmentation of Irg 907 as was shown by CIDNP experiments [24]. The results do not however disclose anything about mechanism of the process. The recent results of Fischer would suggest that ITX in sensitisation of the α-cleavage of Irg 907 by an energy transfer process.

The related experiment showed that NMDEA is a far better synergist than TEA.

EXPERIMENTAL

2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one was obtained from Ciba-Geigy and isopropylthioxanthone (mixture of 2 and 4 isomers) was obtained from International Bio Synthetics. 2-Ethyl-2-(hydromethyl)-1-3-propanediol tri-acrylate, N-methyldiethanolamine, triethylamine and benzophenone (Aldrich) were used as received. The formulations were prepared weight/weight base. UV curing of these films was carried out using a Colodry UV Curing Unit. The medium pressure mercury lamp (100w cm^{-1} and 23 cm in length) was situated 15 cm above a moving belt. The

belt had a variable speed and had been calibrated in a speed of cure in $mmin^{-1}$. The degree of cure for each film was measured arbitrarily using a hard rubber bulb. The film surface was rubbed firmly by rubber bulb. When no visible deformation of the surface occurred, the film was considered cured. This test was repeated on a minimum three samples. The substrate used was Gateway Natural Tracing Paper, GNT (Wiggins Teape Group Ltd.) The formulations were coated on the substrate using 12μ , KBar.

The photopolymerisation was followed using a differential scanning calorimetry, Perkin Elmer DSC-4, to allow irradiation of the sample in the calorimeter chamber. The two ends of a two-branch UV-light conducting fibre had been inserted on the cover of the DSC-4 by drilling holes directly above the samples and reference holders. The two-branch flexible UV light guides (50 cm long each) ended on a ferrule connector which had been plugged into one side of an extended aluminium cylinder. In this aluminium cylinder had been placed a manual shutter to block the incident light at the input end, an interference 365nm filter (International Light NB-365), a solid IR filter (Schott KG-1) and neutral density filters. The extended cylinder assembly had been joined to the water cooling house of a Hanovia Uvitron irradiation system provided with a quartz lens and a 100w high pressure mercury lamp. All the irradiations and measurements were made at 40^{o}.

The DSC was calibrated by the heat of fusion of indium (6.80 cal^{-1}).

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CHAPTER 6

THE CHEMISTRY OF IRG-907

Chapter 6. THE CHEMISTRY OF IRG-907

Irgacure 907 (1) is an unusual photoinitiator in that it possesses a $\pi\pi^*$ triplet state and yet it undergoes Type I cleavage. Presumably the amine substituent reduces the bond strength to such an extent that it lies below the energy of the triplet state.

Irgacure 907 was found to be a highly effective initiator in a number of systems. As mentioned in Chapter 5 of particular interest is whether (1) can also act as a synergist by virtue of it containing a morpholine group. To test this point, N-isopropylmorpholine was synthesised and this was used to generate the amino alkyl radical generated on Type I cleavage.

Using different methods, RTIR, FTIR, DSC and Bulk Polymerisation, the mechanism of the reaction has been probed.

α-Aminoalkylacetophenones

α-Aminoacetophenone derivatives are the most recent type of α-cleavage photoinitiators. The most versatile derivatives are substituted at the 4-position on the benzoyl moiety by strongly electron donating substituents such as alkylthio or dialkylamino groups. This feature induced a red-shift of the main absorption band into the region above 300nm, with the end absorption reaching far into the near UV or even visible range

of the spectra (1). Since their initiating efficiency is very high, they have found widespread use in applications where irradiation at longer wavelengths is crucial. This includes pigmented systems such as printing inks, white lacquers, resist applications and printing plates [1, 2, 3].

Two types of α-aminoketone photoinitiators are very popular (now commercially available), namely 2-methyl-1-[-4-(methylthio)phenyl]-2-morpholino-propan-1-one (MMMP) [1] or Irgacure 907 [3, 4, 5] and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (BDMB) [2] or Irgacure 369 [6]. The structures of both compounds are shown in Fig 6.1

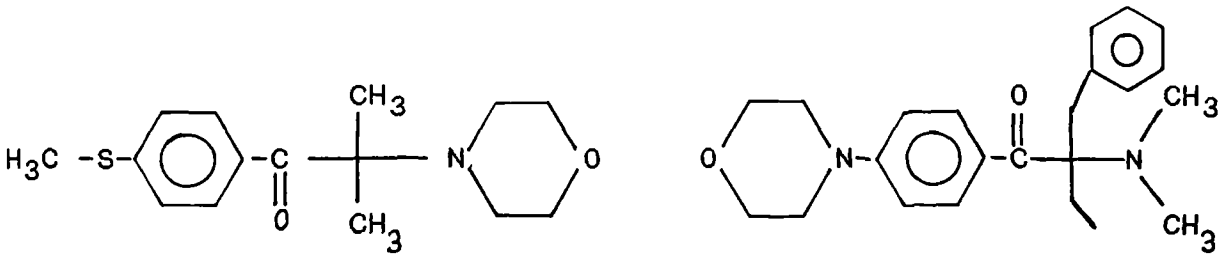


Fig. 6.1

(1) (2)

ABSORPTION CHARACTERISTICS

Compared to the spectra of photoinitiators possessing a non-substituted benzoyl chromophore, the main absorption bands of acetophenone derivatives bearing an alkylthio or amino substituent at the 4-position are strongly red-shifted. Fig.6.2 shows the comparison among the spectra of 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) (Irgacure 651) and MMMP (Irgacure 907) and BDMB (Irgacure 369) [7]

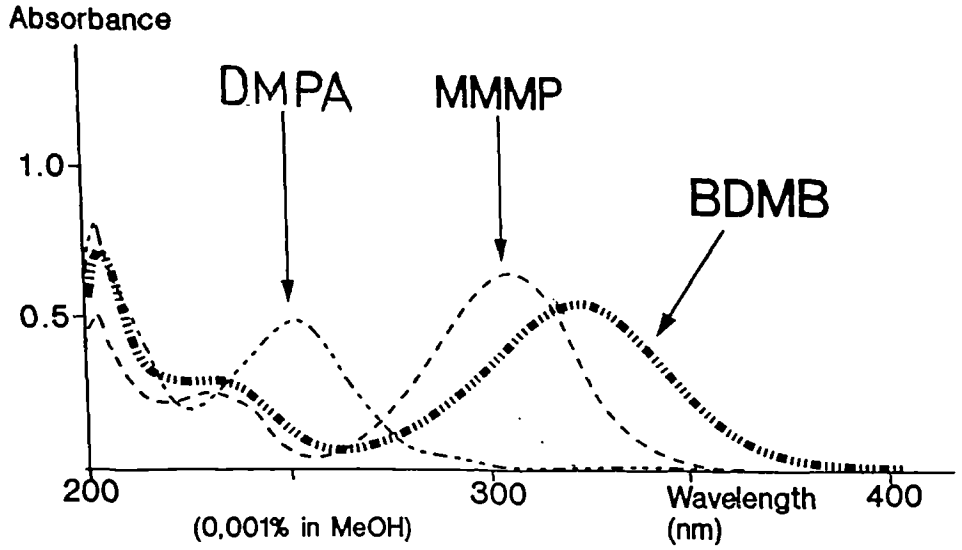


Fig 6.2. Absorption spectra of DMPA (Irg-651), MMMP(Irg-907) and BDMB(Irg-369).

The non-substituted benzoyl chromophore has its main absorption far below 300nm ($\pi \rightarrow \pi^*$ transition at about 240-250nm) and exhibits a low intensity $n \rightarrow \pi^*$ transition band around 320nm.

The introduction of electron donating substituents such as

methoxy, methylthio or amino groups in the para position shifts the main absorption band towards longer wavelengths. The thio or amino substituents induce strong charge transfer characteristics to the excited state and the absorption maxima are now situated around 305 and 322nm respectively.

Irg 907 and Irg 369 undergo α-cleavage as has been unequivocally demonstrated using the technique of chemically induced dynamic nuclear polarisation (ClDNP) and radical-trapping experiments [8, 3]. A further useful aspect of these materials is that their initiation efficiency is increased by sensitisation using thioxanthones as triplet sensitizers. As mentioned in Chapter 1 introduction of the electron-donating substituents methylthio and morpholino into the 4-positions of the benzoyl group in a benzoin lowers the triplet energy to about 60 kcal mol^{-1} and the triplet state character has changed from $n \rightarrow \pi^*$ to $\pi \rightarrow \pi^*$. Efficient Type I cleavage of benzoins is usually associated with the lowest excited triplet state having an $n \rightarrow \pi^*$ character [10]. (This raises the question as to why 1 and 2 undergo α-cleavage?). The cleavage process produces α-amino alkyl radicals which are likely to be more stable than α-alkoxyalkyl radicals and consequently the bond which cleaves in Irg 907 and Irg 369 is weaker than that in a typical benzoin ether.

If the C-C bond energy in Irg 907 and Irg 369 is lower than

60 kcal mol^{-1}, it would answer the question as to why 1 and 2 undergo α-cleavage. But it is not so easy to see how the excited π-π^* triplet state energises this bond.

Sensitisation

CIDNP and trapping experiments on the sensitised photodecomposition of photoinitiator Irg 907 demonstrated the formation of the 4-methyl thiobenzoyl radical [2]. These results were interpreted by two parallel reaction pathways:

(1) Energy transfer from the excited-state sensitiser to the photoinitiator would produce a triplet-state α-amino-ketone, which subsequently undergoes the same Norrish I reaction as upon irradiation without sensitiser.

(2) Electron transfer from the α-amino ketone to the excited sensitiser would lead to other reaction products. The benzoyl radicals formed via the energy transfer route act as initiating species for the polymerisation process. These σ-radicals are well-known to add efficiently to vinylic double bond [11].

Sensitisation in Benzene [12]

A time resolved CIDNP spectrum of an irradiated sample of a

mixture of the α-amino ketone Irg 907 and thioxanthone (T) in benzene, showed a strong signal at 9.64 ppm vs TMS and is attributed to the aldehyde proton of 4-(methylthio)benzaldehyde (4). The formation of the aldehyde and the enamine can be explained by an in-cage disproportionation of the radical pair i, as it was found for the Norrish I reaction occurring upon direct irradiation of this photoinitiator (Fig 6.3) [12].

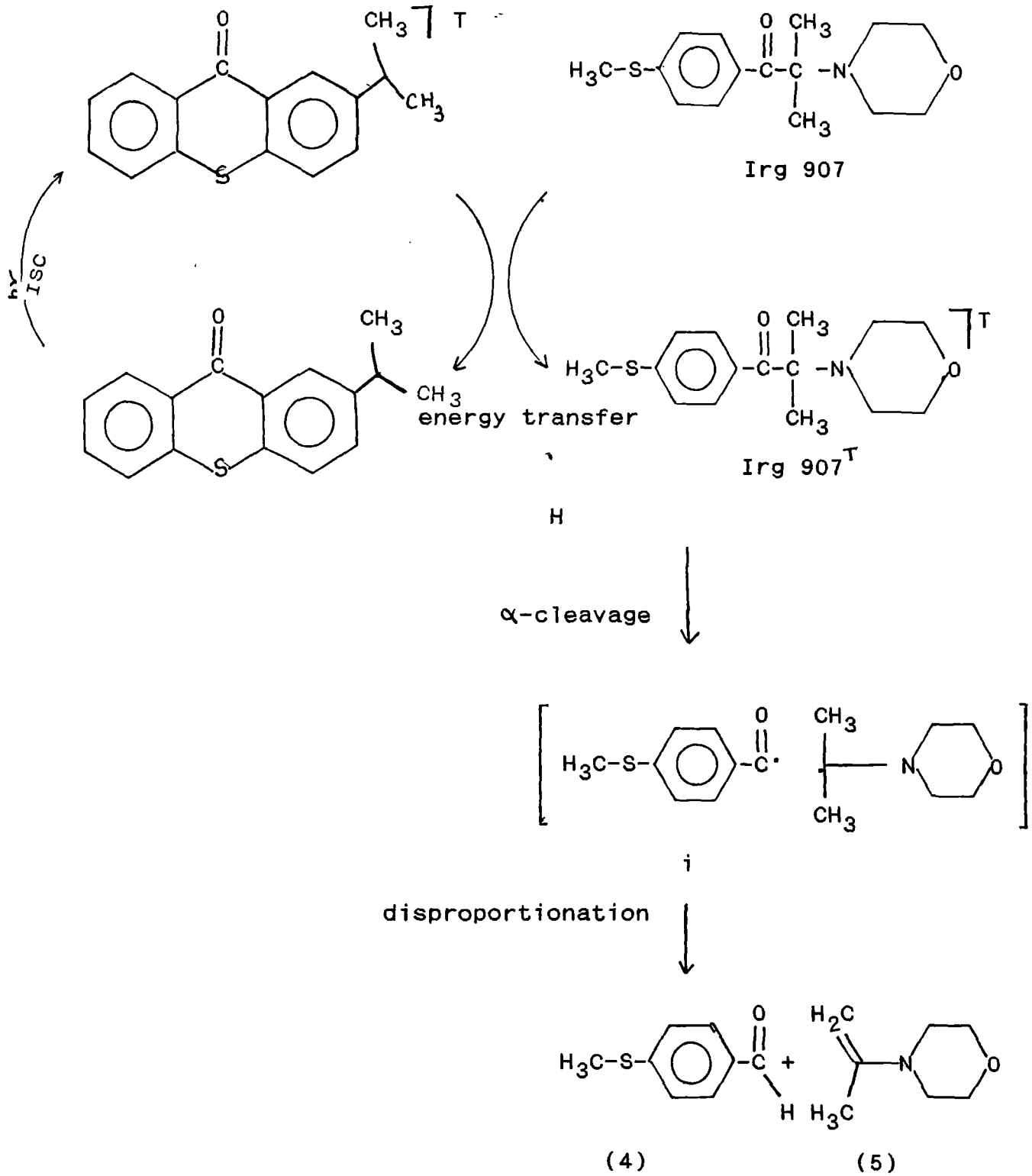
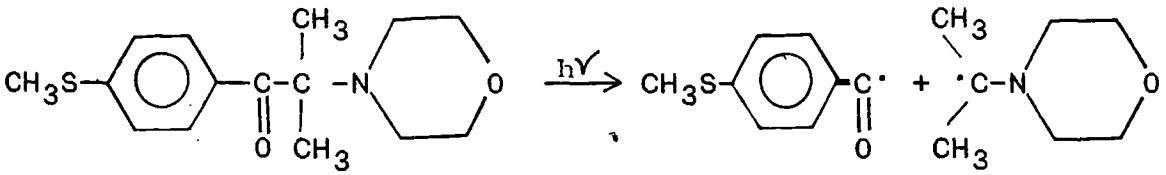


Fig 6.3 α-Cleavage of photoinitiator MMMB (Irgacure 907) induced by energy transfer

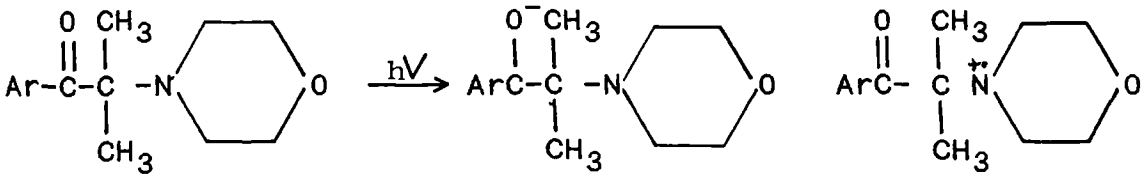
RESULTS AND DISCUSSION

Irg 907 has been shown by ClDNP [4, 12, 13, 14] and radical trapping experiments [9] to fragment in the following fashion scheme.

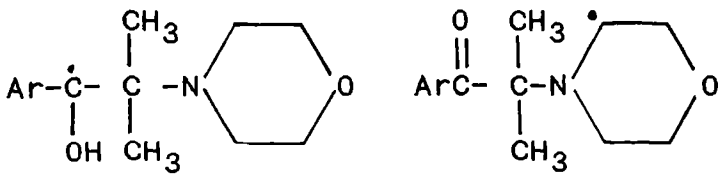


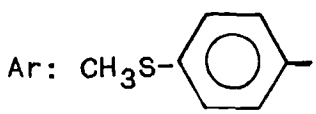
Scheme

Since the initiator is an amine this raised the question as to whether the initiator can act as its own amine synergist. Such a scenario has in fact been described and the claim made that the morpholino group acts as a hydrogen donor [15, 16].



Quenching





Initiates polymerisation

The synergistic properties of N-isopropylmorpholine (1PM) were studied to test this claim. As mentioned before, different methods were employed to test the synergistic properties of 1PM.

(1) Using FT1R spectroscopy to measure the residual unsaturation in polymer films.

Following the conversion of a coating formulation from a liquid to the solid state using UV light, one needs to determine the extent to which the UV initiated polymerisation of the unsaturated compound has proceeded. This is normally determined by measuring the "degree of cure". The degree of cure is a widely used term which usually refers to the number of double bonds consumed during the polymerisation reaction. In practice, the degree of cure for surface coatings is mostly determined by empirical tests [17], such as solvent resistance, abrasion, pencil hardness and thumb twist test. These tests provide at best, qualitative results because they are dependent upon the operator. Such physical methods also give an indication of the extent of crosslinking which has occurred with increasing irradiation, but not about the number of residual double bonds at the coating surface, substrate interface or throughout the bulk of the film.

In order to study what changes occur at or near the film surface, the analytical technique of Fourier transform infrared spectroscopy (FTIR), in conjunction with transmission and ATR measurements was applied.

This technique offers many possibilities to study the amount of cure in surface coatings and is proving to be one of the unique analytical tools for the characterisation of coatings [18]. The synergistic efficiency of IPM and NMDEA, were compared by studying their effect upon curing reactions initiated by ITX and Irg-907 using a trifunctional acrylate as the polymerisable material. These reactions were conveniently monitored by FTIR.

Different concentrations of N-isopropylmorpholine (IPM) were used to see the synergistic effect. The results are recorded as the percentage of residual double bonds remaining after UV irradiation. The samples are:-

H0	:	2% Irg-907	H2	:	2% ITX
		TMPTA			1% NMDEA
					TMPTA
H1	:	2% Irg-907	H3	:	2% Irg-907
		10% NMDEA			1% IPM
		TMPTA			TMPTA

H4 : 2% Irg-907 H5 : 2% ITX

10% IPM 10% IPM

TMPTA TMPTA

As can be seen clearly from Fig.6.4 the residual unsaturation was very high, (44%) when IPM was used as a synergist with Irg-907 which is Type I initiator. The same high unsaturation was observed in the case of ITX, (36%) which is well known as a Type II initiator.

When NMDEA was used instead of IPM, the results were quite different. The residual unsaturation dropped very efficiently with either Irg-907 or ITX.

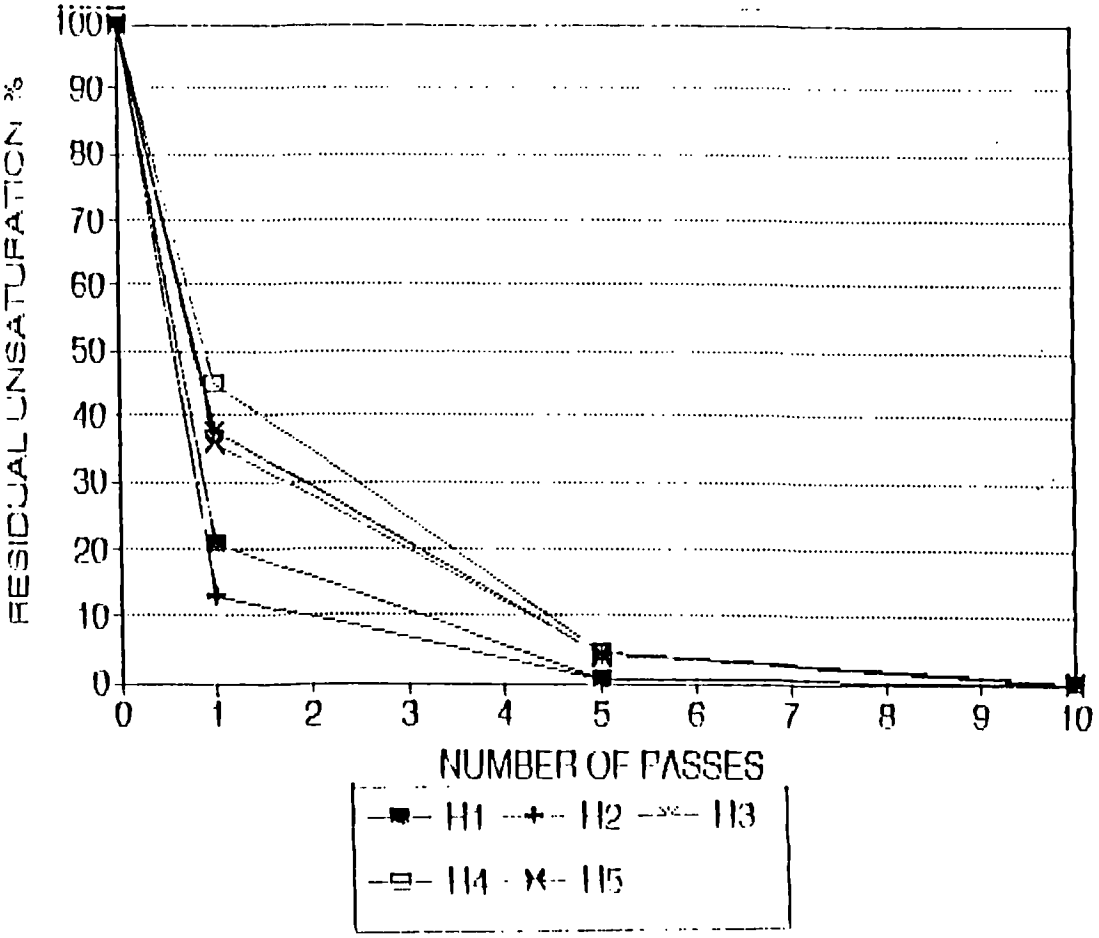


Fig 6.4.The residual unsaturation % of samples H1-H5 from RTIR Spectroscopy.

Similar results were obtained in bulk polymerisation and RTIR spectroscopy experiments. In bulk polymerisation experiments in Fig 6.5 and in Figs 6.6 and 6.7 it was found that little polymerisation of trimethylolpropane triacrylate (TMPTA) occurred when IPM was used as synergist with the efficient Type II initiator isopropylthioxanthone (ITX). When N-methyldiethanolamine was used efficient polymerisation was observed. Irgacure 907, being a Type I photoinitiator initiated the polymerisation of TMPTA efficiently in the absence of amine. The addition of NMDEA had a marginally beneficial effect probably due to oxygen scavenging where IPM failed to produce any effect.

The samples are:

X1 : ITX/IPM / TMPTA

X2 : ITX/NMDEA / TMPTA

X3 : Irg-907 / TMPTA

X4 : Irg-907/NMDEA / TMPTA

X5 : Irg-907/IPM / TMPTA

X6 : BP / TMPTA

X7 : BP/IPM /TMPTA

X8 : BP/NMDEA / TMPTA

X9 : Irg-651 / TMPTA

X10 : Irg-651/IPM / TMPTA

X11 : Irg-651/NMDEA / TMPTA

(The concentration of IPM was 1.1% and the concentration of NMDEA was 1.3%)

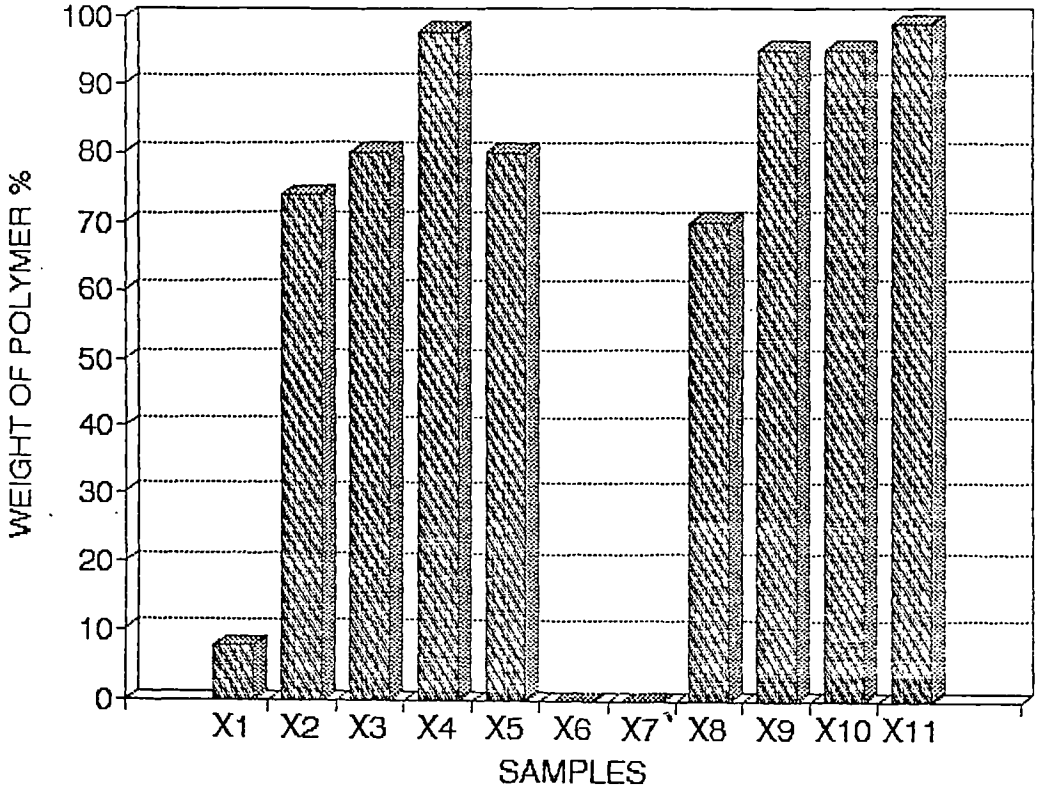


Fig 6.5. Bulk Polymerisation Results of samples X1-X11.

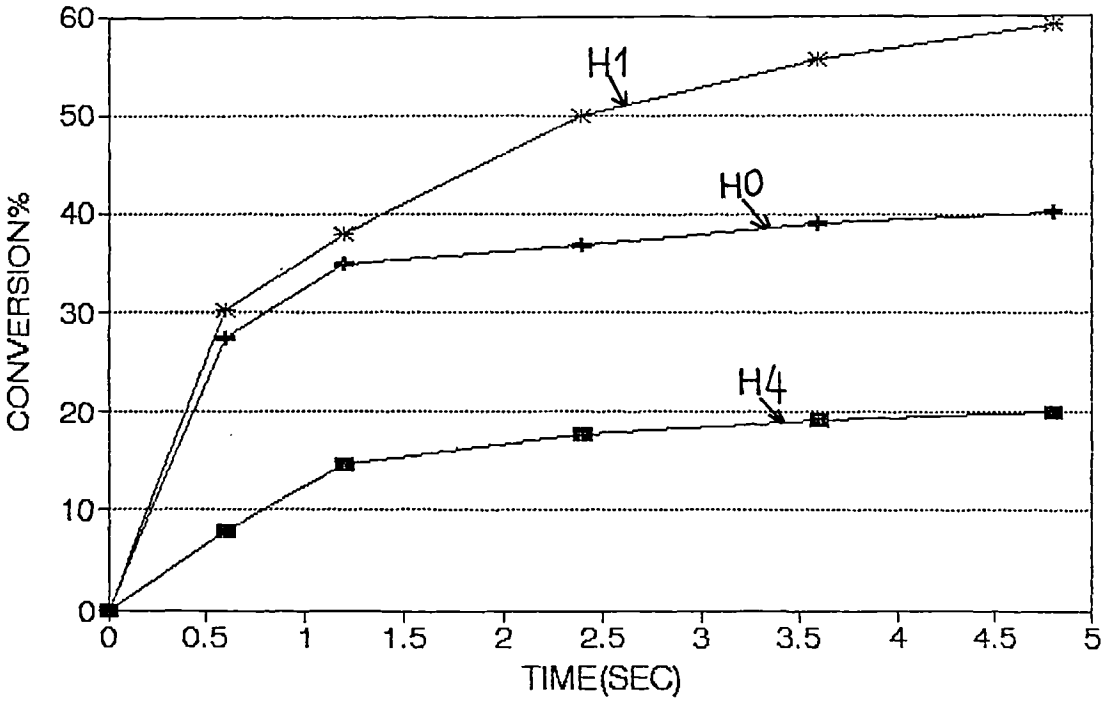


Fig 6.6. Conversion % of samples H0,H1,H4 from RTIR Spectroscopy during 5 sec of irradiation.

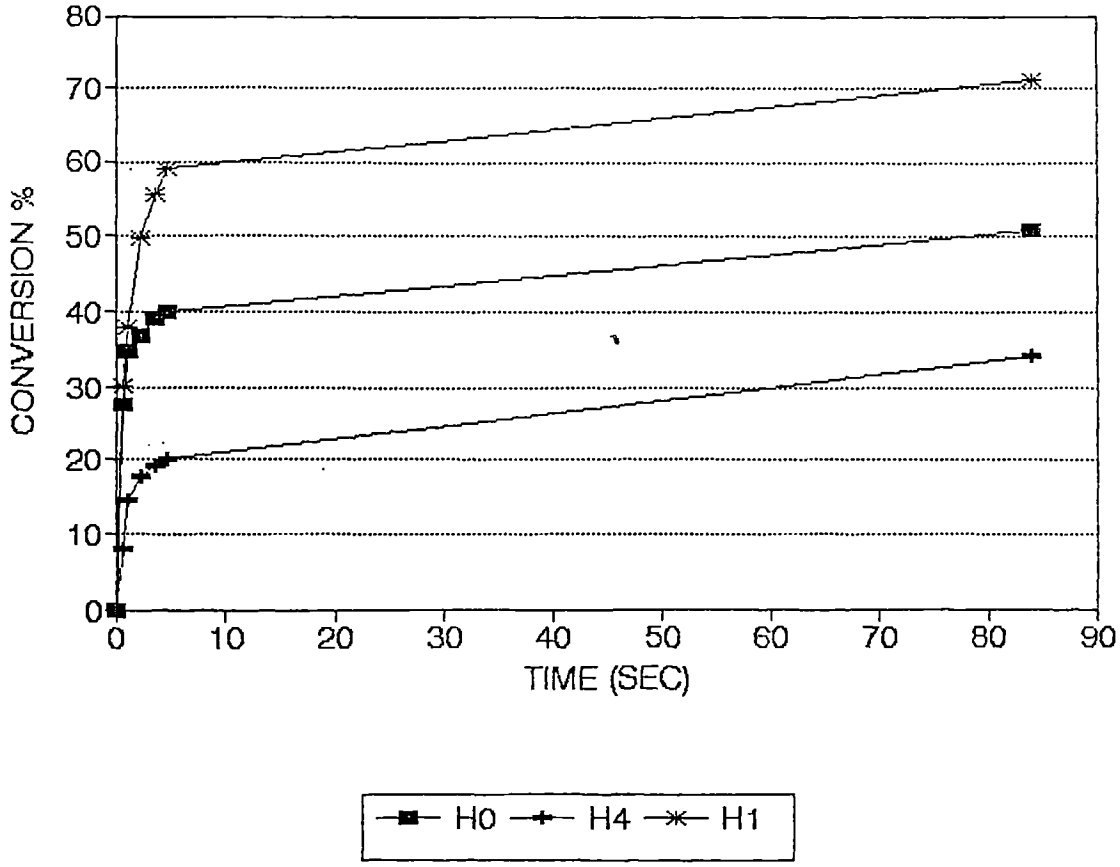


Fig 6.7. Conversion % of samples H0,H1,H4 from RTIR Spectroscopy during 80 sec of irradiation.

That IPM is a grossly inefficient synergist was proved by an experiment using Type II photoinitiators, thioxanthones and benzophenone in conjunction with IPM for the curing of thin films. Benzophenone - IPM and benzophenone-N-methyldiethanol-amine were irradiated with 100w medium pressure mercury lamp during 140 sec. The conversion of IPM-BP system was 12% where the BP-NMDEA reached 70%.

Using another technique photo-differential scanning calorimetry (photo DSC) [13, 20] it was shown that high concentrations of IPM can quench the Type I cleavage of Irg-907, as shown in Figs.6.8, 6.9 and 6.10. From Fig. 6.8, the heat flow of Irg 907/LA was nearly 15mW. Adding 10% to this sample, dropped the heat flow to 5mW, when the concentration of IPM was increased to 15% and then to 20%, the heat flow reduced to 1%.

The triplet of the ketone, from which reactions occur as demonstrated by ClDNP experiments [24] has an estimated lifetime of <10n sec. If used in curing experiments at 3% level this equates to a concentration of $\sim 10^{-1}$M and it is possible that some bimolecular reactions may ensue between a molecule in its triplet state and one in its ground state.

As shown in Figs.6.8, 6.9 and 6.10, 10, 15 and 20% of IPM was used in laurylacrylate monomer and 2% of Irgacure 907 was added. From the results, high concentration of IPM quenched the polymerisation when Irgacure 907 was used as a photoinitiator. Without IPM, the formulation of Irg-907 with laurylacrylate gave very good exotherm; the addition of 10% of IPM changed the character of exotherm very effectively. In these formulations IPM acted as a physical quencher of triplet states of Irgacure 907 and was a most inefficient hydrogen donor. Similar results were obtained in lower concentrations of IPM.

One of the most efficient hydrogen donors, N-methyldiethanol-amine (NMDEA) was used in the same concentration of IPM and the exotherms for reaction mixtures containing this amine were compared with these where IPM had been used (Figs. 6.10 and 6.12) When N-methyldiethanol amine was used, efficient polymerisation was observed. The heat flow reached to 65 mW at the same concentration of IPM and gave 1mW of heat.

Another well known Type I photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone (Irgacure 651) was used to test the efficiency of IPM. 1%, 3% and 5% of IPM was used with 2% of Irgacure 651 in laurylacrylate. The results are shown in Figs 6.13, 6.14 & 6.15 respectively .

As can be readily seen from the Figures, higher concentration of IPM increased the heatflow and it reached 57 mW for 5% IPM. The IPM is not quenching the triplet state of the initiator which is Irg -651 , probably due to the triplet lifetime of Irgacure 651 is very low. The value is estimated [21] to be lower than 0.1 ns. This is, in fact, too short to be accurately determined even using modern fast time resolution techniques. This extremely short lifetime precludes bimolecular reactions such as hydrogen abstraction and quenching and therefore the only function of IPM in this system must be as an oxygen scavenger.

The photoreduction of benzophenone by (isopropylmorpholine) (IPM) was investigated in acetonitrile solution using 350nm radiation. The solution which was 10^{-5}M of benzophenone

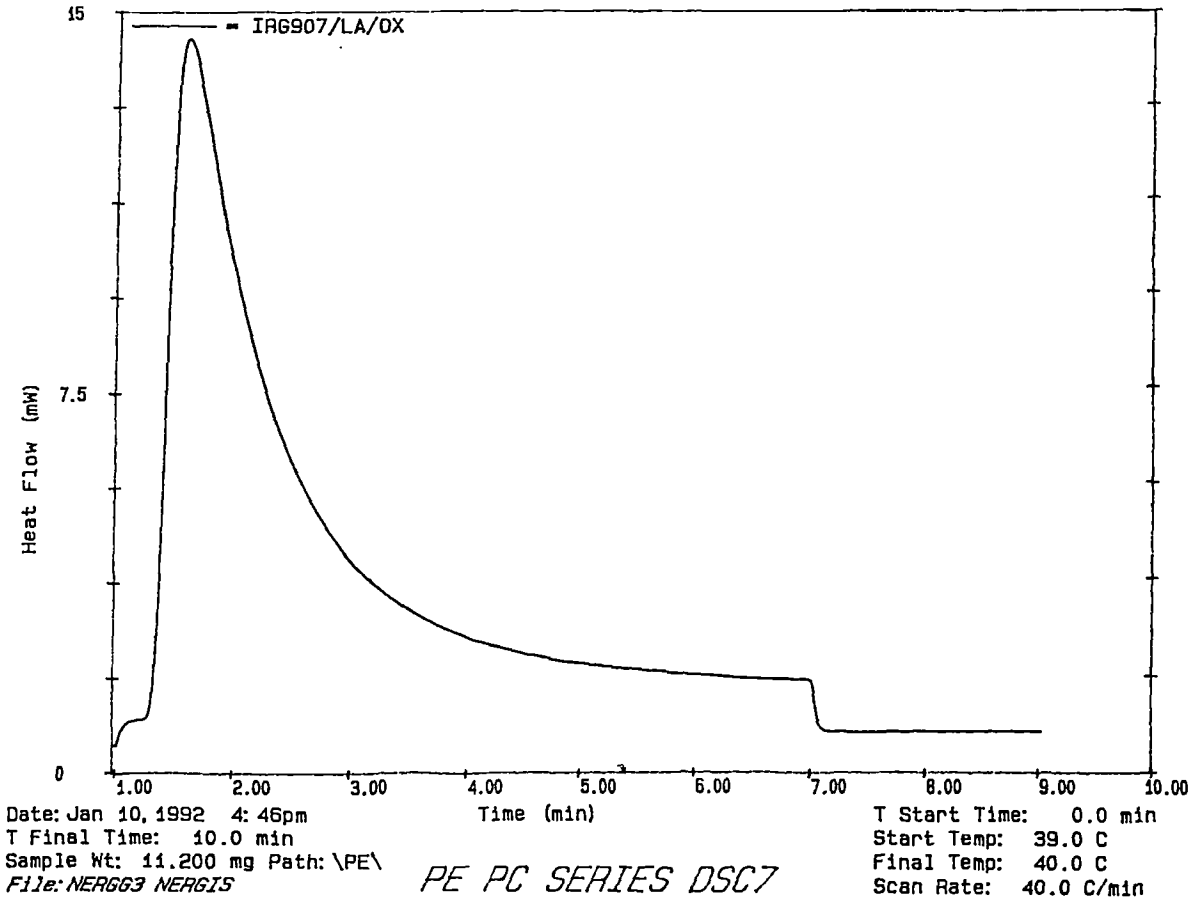


Fig 6.8. DSC trace for photopolymerisation of 2% IRG-907/LA.

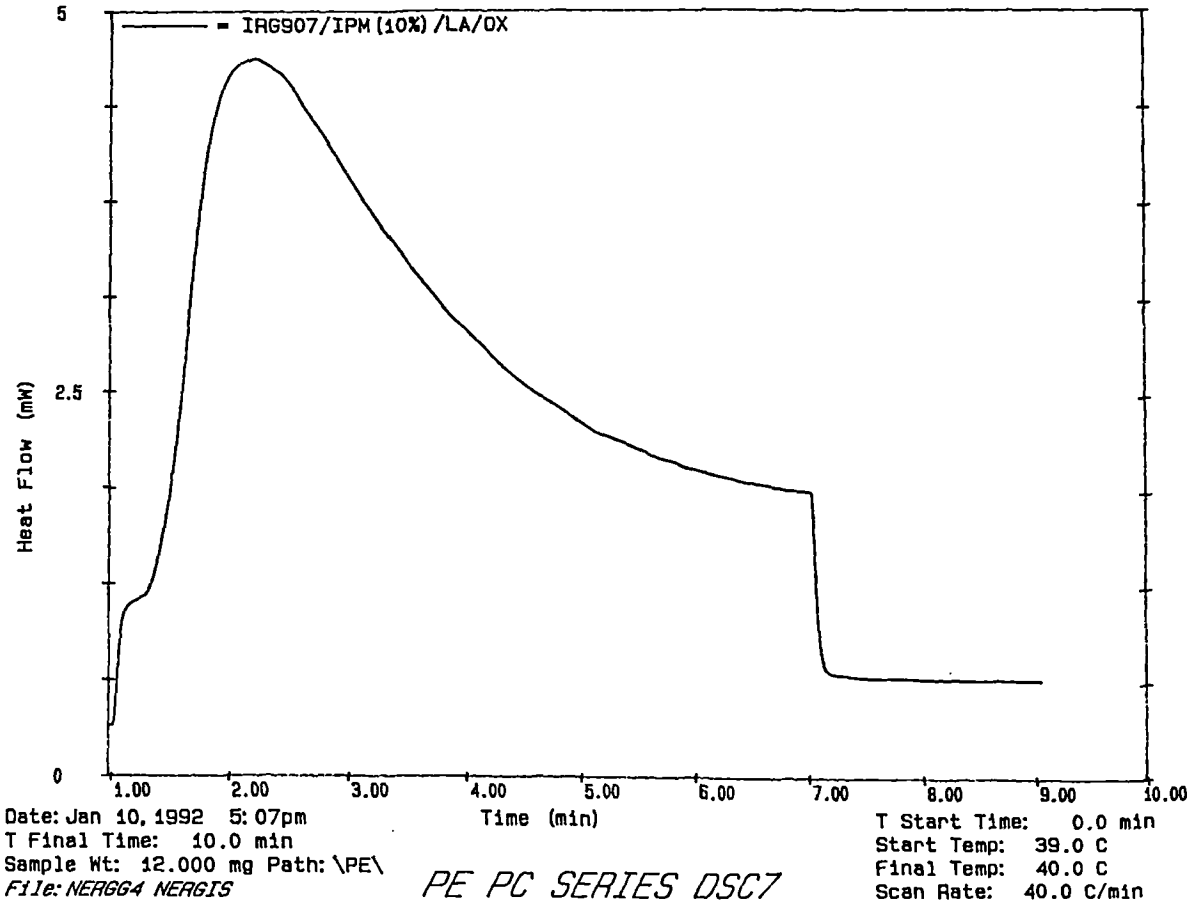


Fig 6.9. DSC TRACE for photopolymerisation of 2% IRG-907/10% IPM/LA.

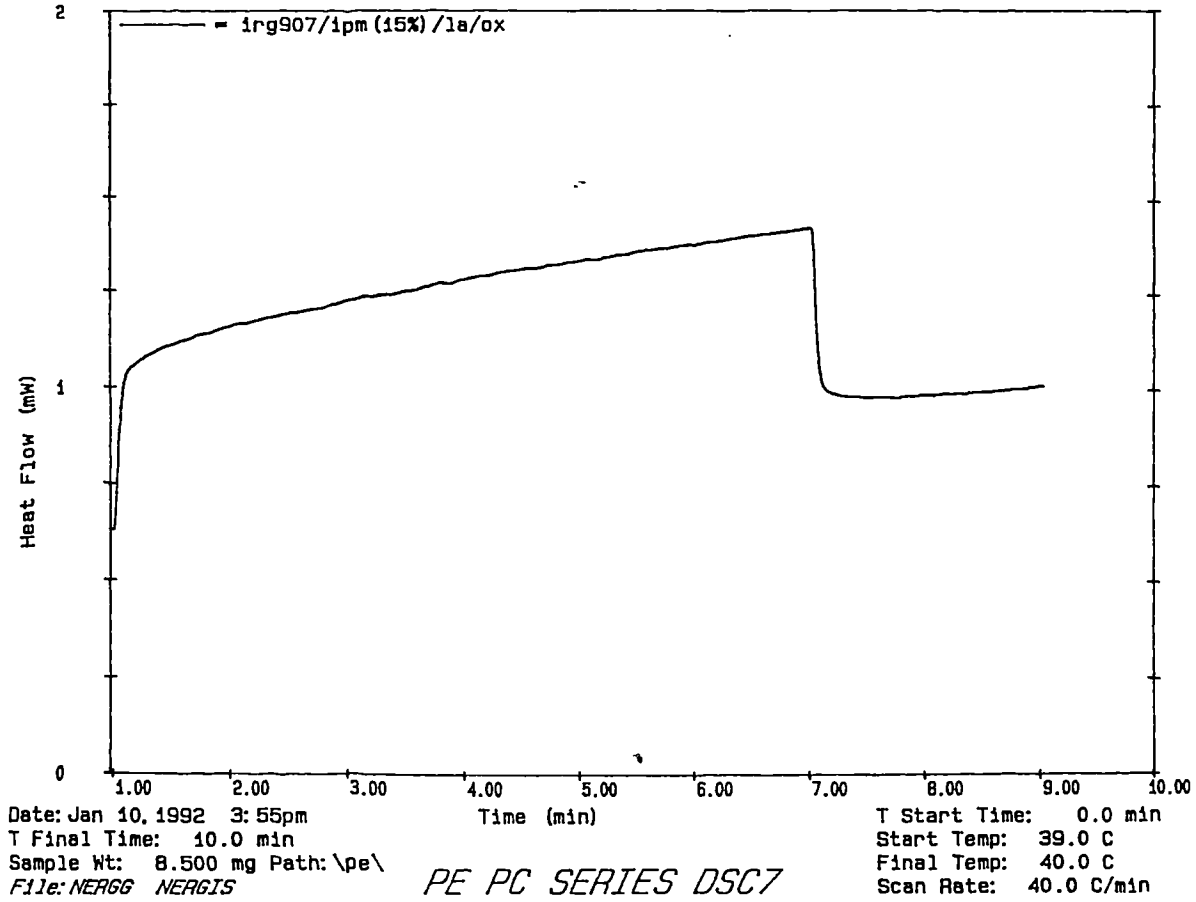


Fig 6.10. DSC trace of photopolymerisation of 2% IRG-907/15% IPM/ LA.

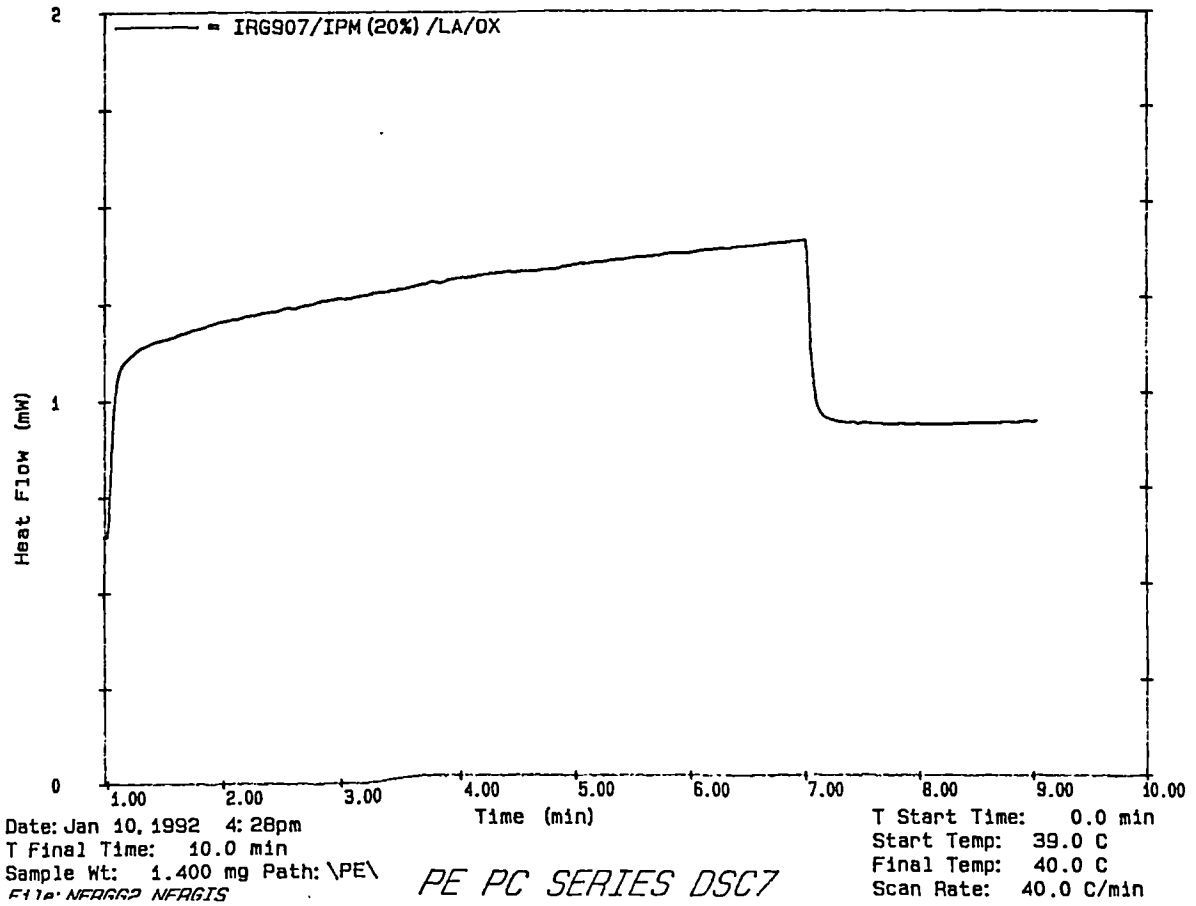


Fig 6.11. DSC trace of photopolymerisation of 2%IRG-907/20% IPM/LA.

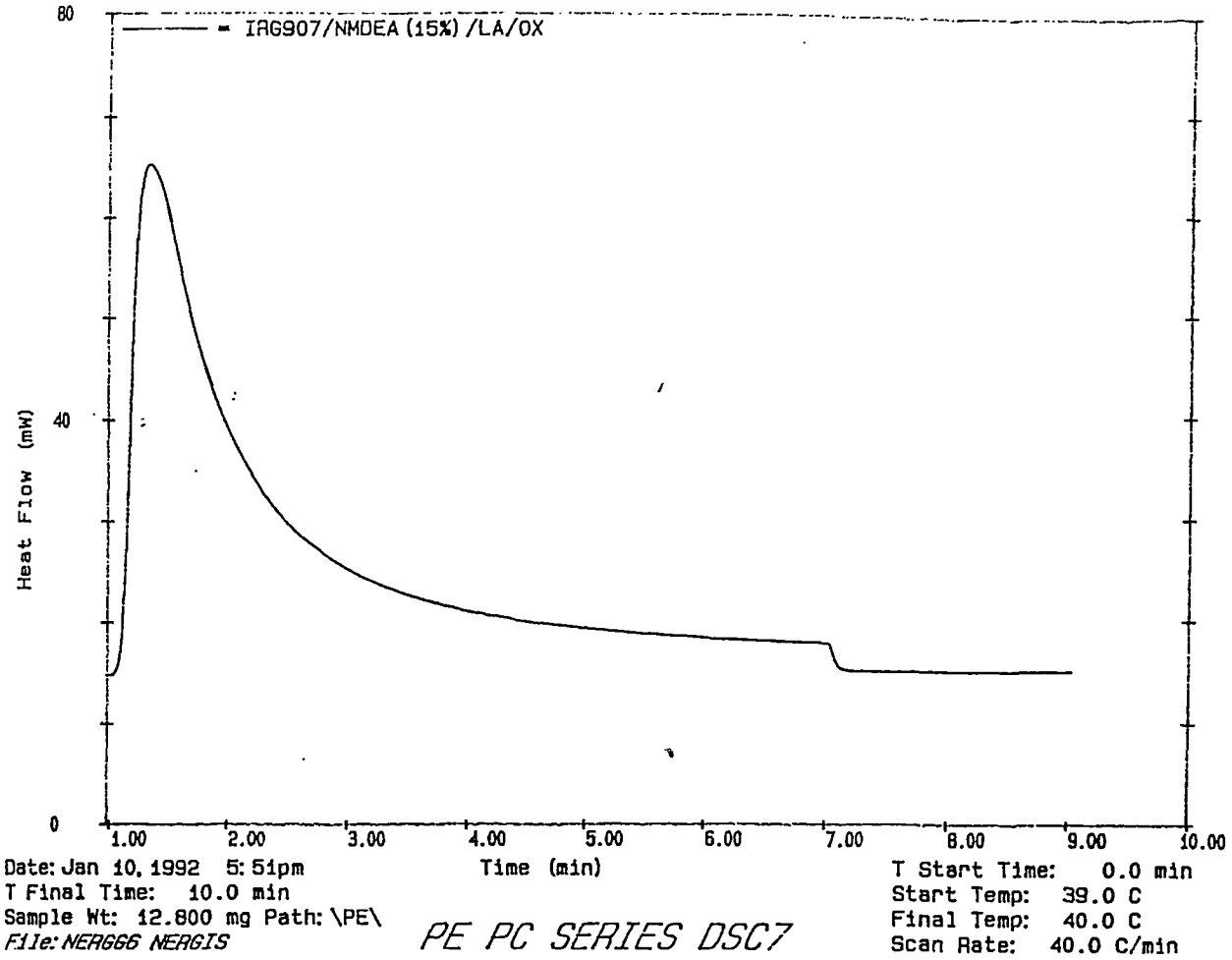


Fig 6.12. DSC trace of photopolymerisation of 2% IRG-907/ 10% NMDEA.

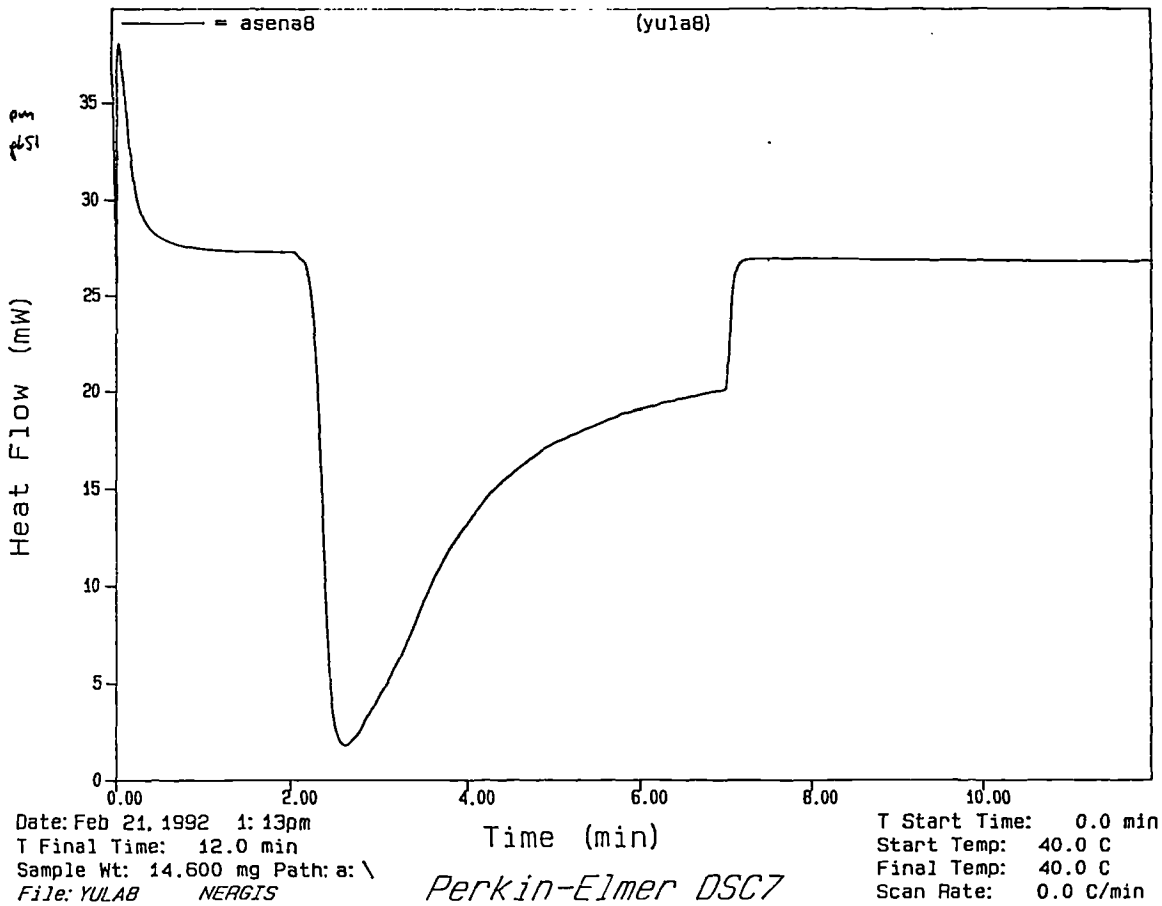


Fig 6.13. DSC trace of photopolymerisation of 2% IRG-651/1% IPM/LA.

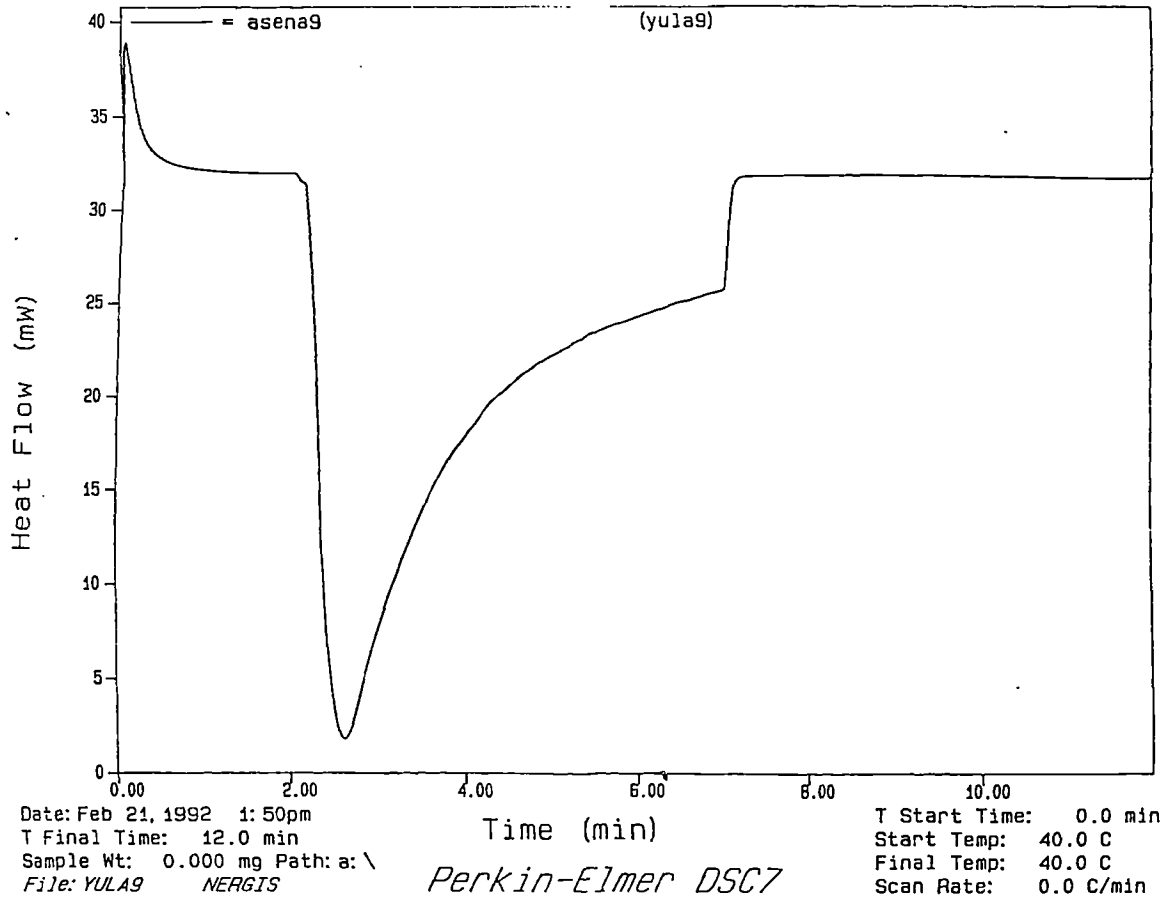


Fig 6.14. DSC trace of photopolymerisation of 2% IRG-651/3% IPM/LA.

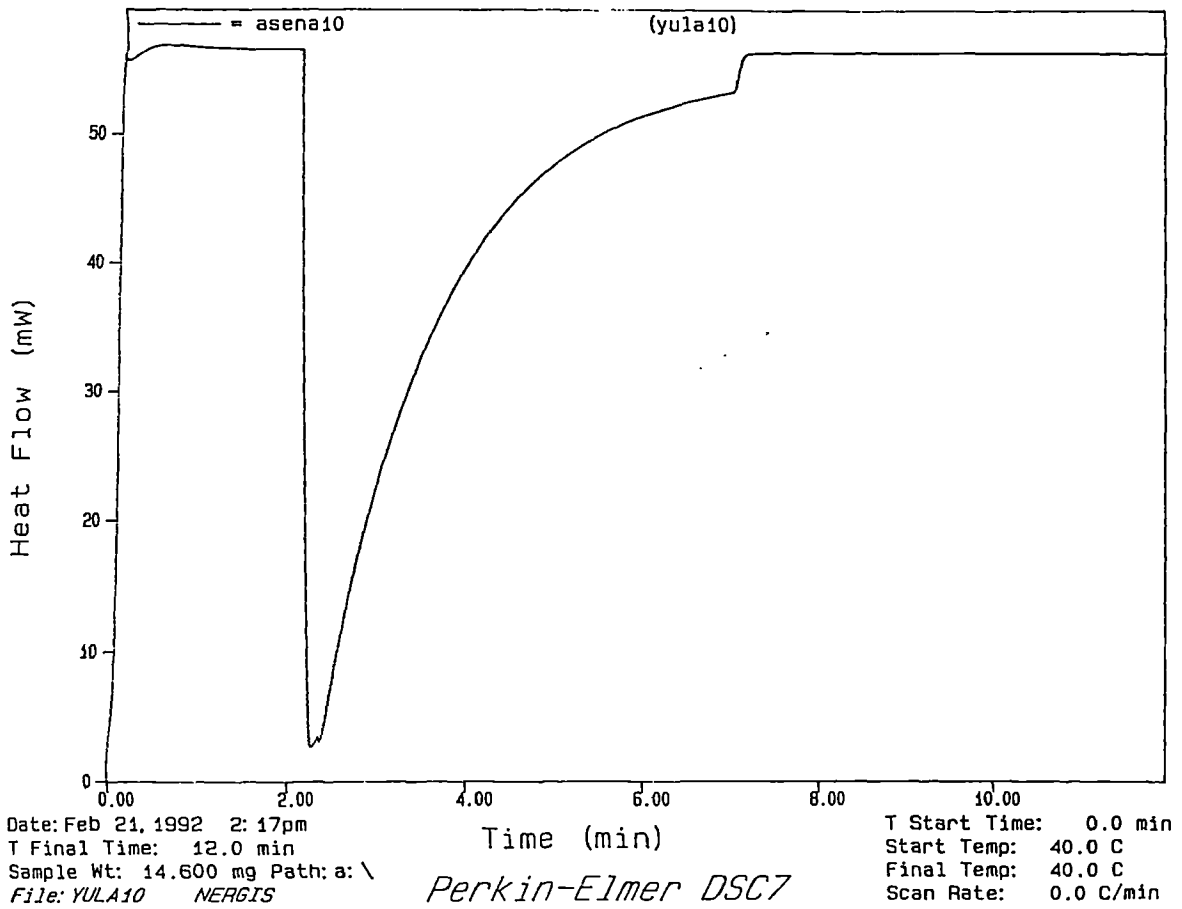
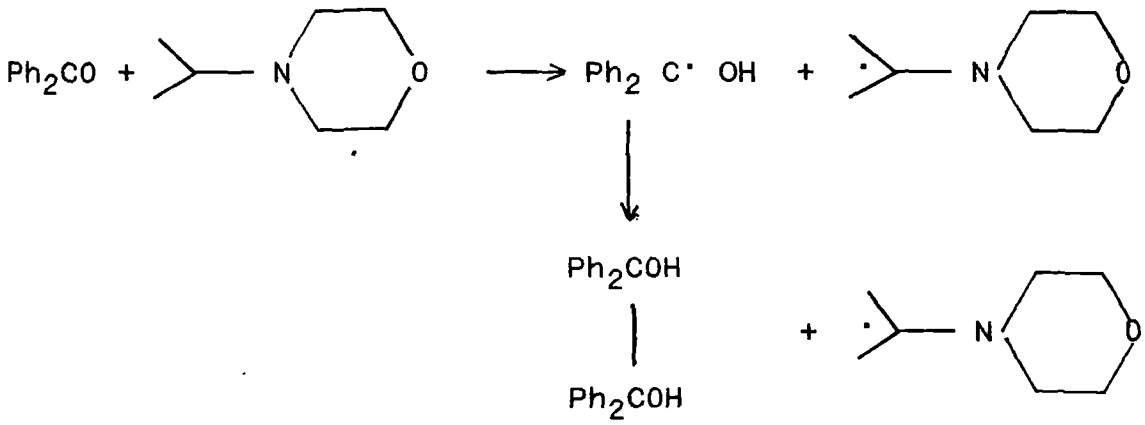
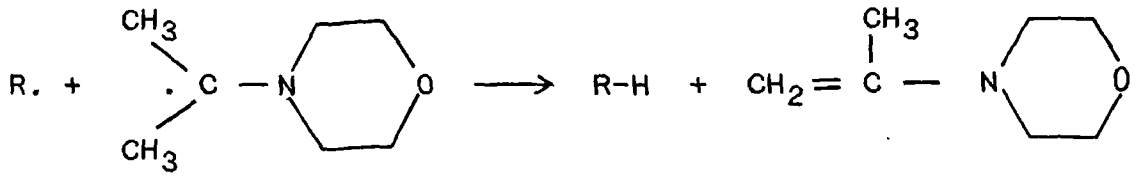


Fig 6.15. DSC trace of photopolymerisation of 2% IRG-651/5% IPM/LA.

and 10^{-5}M of IPM was irradiated for two hours. The reaction was followed by gas liquid chromatography and then GC-MS . No product peak was observed with either GLC or GC-MS . These results were confirmed. Our findings were that IPM is a grossly inefficient synergist was proved by experiment using Type II photoinitiators.

The possible reaction between benzophenone and isopropyl morpholine is as shown:[1]





(1)

In conclusion; we have presented evidence that 1PM can act as a quencher of the triplet state of 2-methyl-1-[4-(methylthio)-phenyl]-2-morpholino-propan-1-one, (Irg-907). It appears to act mainly as a physical quencher since it is incapable of reducing the triplet state of ITX and BP.

Using 1PM as a model for the amine containing part (Irg-907) it appears that the morpholino group present in (Irg-907) will act as a physical quencher and it is a very poor hydrogen donor.

EXPERIMENTAL

The materials:

Isopropylmorpholine was synthesised according to the method previously described in Chapter 2 .

Laurylacrylate was obtained from Lancester Chemicals Company.

Irradiation:

10 cm^3 solutions were irradiated in Pyrex tubes (26.0 x 1.9 cm) and continually flushed with nitrogen during irradiation by a circular array of sixteen 8-w black-light fluorescent lamps (Sylvania FT 875/BLB) starting from 2 hours to 10 hours.

Preparation of Solutions for Irradiation

The solution was prepared 10^{-5}M of benzophenone and 10^{-5}M of isopropylmorpholine in acetonitrile (50 cm^{-3}). An internal standard was added to the solution for the g.l.c. analysis.

The gas liquid chromatography (GLC) experiments were performed on a Perkin-Elmer ∇3 Gas Chromatograph with a Flame Ionisation Detector using a temperature programme (range 60^{o}-230^{o}C at a rate of 10^{o}C min^{-1}). The separations were performed on a 15m fused silica column (internal diameter 0.32 mm) containing DB-5, with nitrogen as the carrier gas.

The mass spectra were recorded on a Finnegan MAT 212 (EI) mass spectrometer (mass range 10-900, scan rate 1.1 sec per dec, resolution 800) which was interfaced with a Varian 3700 gas chromatograph. A temperature programme was used for the separations (range 70-230^{o}C at a rate of 10^{o}C min^{-1}) which were performed on a 15m fused silica column (wide bore 1.5 m) containing DB-5 (95% dimethyl-5% diphenyl-, polysiloxane); the carrier gas used was helium.

Bulk Polymerisation:

Experiments were carried out as described previously in Chapter 3.

The concentration of IPM was 1.1% and the concentration of NMDEA was 1.3% where the initiator concentration was 0.2%. Trimethylolpropane triacrylate was used as monomer.

Perkin -Elmer Isothermal DSC 7:

Was used to determine the DSC results. Irradiation time was 10 min. The starting temperature entered was 39.0 °C and the final temperature was given as 40.0 °C and the scan rate was 40.o °C/min. This method is described in more detail in Chapter 5.

FTIR Experiments:

The films were coated on GNT paper. The film thickness was 12 μ The spectra were recorded for each sample before and after irradiation . On exposure to UV irradiation the consumption of carbon carbon double bonds of the acrylate group was monitored by the
peak at 810 cm^{-1} associated with the CH deformation of the vinyl group and the doublet at 1640 cm^{-1} and 1620 cm^{-1} associated with the carbon carbon double bond stretch and the overtone frequency at 810 cm^{-1} respectively. The area associated with each peak was computed given a predefined baseline, and from which peak ratio's were evaluated and the percentage of a given peak calculated. The number of residual double bonds associated with each variable peak were calculated.

RTIR experiments were carried out according to the method described previously in chapter 4 .

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CHAPTER 7

PHOTOINDUCED FRAGMENTATION OF AMINOALCOHOLS

Chapter 7. PHOTOINDUCED FRAGMENTATION OF AMINOALCOHOLS BY QUINOXALINES

Tertiary amines can fulfil two roles in the curing of UV systems by a free radical route. They can scavenge peroxy intermediates formed by the reaction of oxygen with radical sites or as the corresponding α-aminoalkyl radicals, they can react with oxygen, thereby reducing the retarding effect of oxygen on the rate of cure.

Possible mechanisms for oxygen scavenging reactions between amines, excited amines and amine radicals with oxygen have been discussed by Davidson [1] and Turro [2] etc.

Mixtures of compounds which possess a low ionisation potential (electron donors) and those having a high electron affinity (electron acceptors) can absorb at wavelengths not characteristic of either.

This absorption is due to an EDA (Electron Donor Acceptor) complex or charge transfer complex. Photochemical reactions have the potential to occur from the excited singlet state without the formation of an excited triplet state formed via intersystem crossing. The close proximity of the components within the excited complex allows the molecules to interact within the relatively very short lifetime of the excited singlet state.

The intermediate states which may lead to a chemical reaction have been summarised by Davidson [2] in Fig.7.1.

Reaction either occurs from the Franck-Condon excited state (possessing the same nuclear structure as the ground state) or from a relaxed equilibrium excited state.

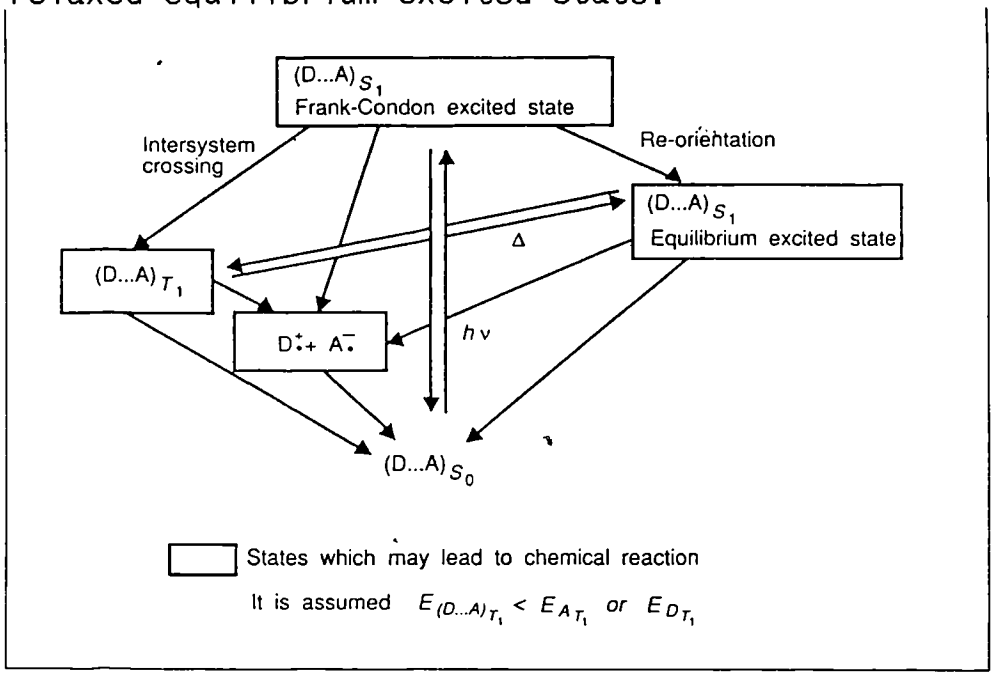


Figure 7.1 Intermediate States of a Charge Transfer Complex which may lead to Chemical Reaction

The majority of an excited state complex formation involves some degree of charge transfer. The formation of an excited complex through charge transfer and the subsequent potential mechanisms which can occur are shown in Fig. 7.2

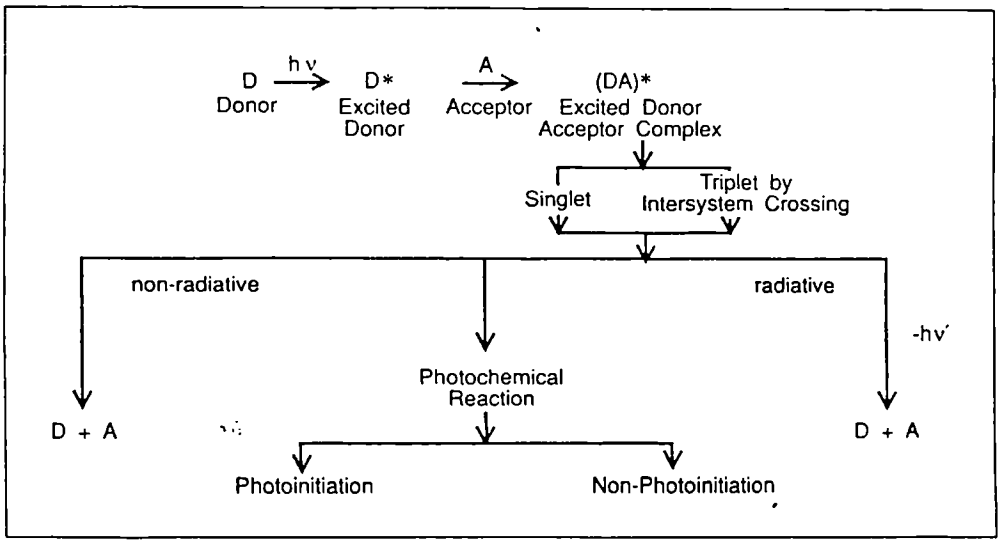


Figure 7.2 Possible Reactions of an Excited Complex

The term exciplex is frequently used in conjunction with excited state complexes. If two or more molecules act co-operatively to absorb a photon, this is an absorption complex. If this complex is capable of emitting a photon, then it can be called an "exciplex". If both components of the exciplex are of the same chemical type, then the exciplex is termed an excimer.

There are other definitions of an exciplex. Davidson [2] defines it as an electronically excited molecular complex of definite stoichiometry. This definition includes excited charge transfer complexes where the ground state complex is excited.

The exciplex may be treated as a stoichiometric species and its reactions can be considered unimolecular in nature, although bimolecular reactions are involved in the formation of an exciplex.

In a similar manner to that of excited ground state complex formation, it is possible to compare the potential chemical reactions of the excited complex which could possibly occur as shown in Fig. 7.3.

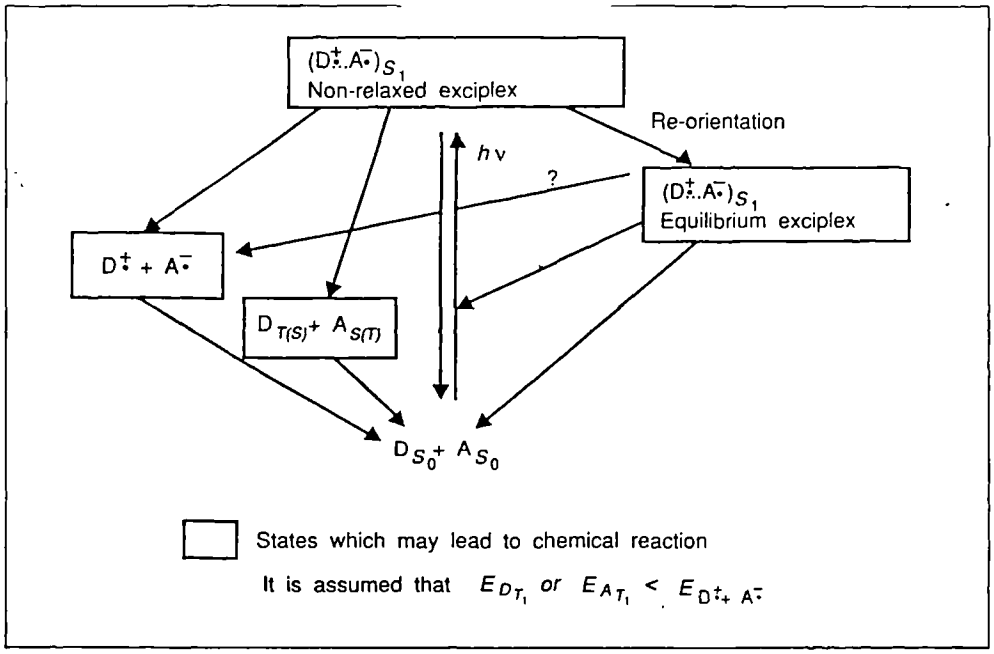


Figure 7.3 Potential Reactions Leading to Chemical Reaction for an Excited State Complex

Initially a non-relaxed exciplex is formed. This can then form radical ions (D^{+}. and A^{-}.) an equilibrium exciplex, or it can dissociate to eventually form the original components of the exciplex.

The feasibility of electron transfer occurring can be ascertained from a knowledge of the ionisation potential of the donor, the electron affinity of the acceptor, the excitation energy of the sensitiser and solvent properties of the medium [3]. A good working equation to employ is the Rehm-Weller equation [4].

$$E_{(D-A)} = I_D - E_{A_A} - C$$

Where

I_D = Ionisation potential of donor

E_{A_A} = Electron affinity of acceptor

C = Coulombic Energy term

In solution, the rates of reaction can only be at maximum, the diffusion controlled rate limit unless there is association between the ground state prior to excitation. The diffusion controlled limit is directly related to the viscosity of the medium and this has really important consequences for radiation curing, since as curing occurs so the viscosity increases. This argument predicts that bimolecular reactions between sensitiser and amine and of amine radicals with oxygen will fall off in effectiveness as the curing process proceeds.

It has been found that the α- and β- aminoalcohols are unreactive under direct photolysis, but they are quite reactive when solutions containing the α-β-aminoalcohols together with various electron acceptors having strong absorption in the near ultraviolet or visible light are irradiated at wavelengths absorbed only by the electron acceptors [5]. Electron acceptors that can be used to promote reaction include thioindigo (TI), a number of polypyridyl-ruthenium complexes, cyanoaromatics, various quinoxalines and quinones. The overall reaction of the α-β-aminoalcohol is remarkably independent of the acceptor used and its excited state multiplicity; however, the quantum efficiency of the process is strongly acceptor dependent [5].

Among the various reactions of the photogenerated radical ion pairs, fragmentation via C-C bond cleavage has been shown to be

a prominent and often clean path for aminoalcohols and amino ketones [6-11].

Irradiation of electron acceptors such as 9,10-dicyanoanthracene (DCA) in the presence of the aminoketone 3-methyl-3-(4-morpholinyl)-2-butanone and water in nonpolar solvents has been found to lead to oxidative cleavage of the aminoketone to form ultimately 4-acetylmorpholine and acetone, together with 9,10-dihydro-9,10-dicyanoanthracene.

A mechanism can be developed whereby single electron transfer quenching of the excited DCA is followed by a nucleophilic attack on the acyl carbon of the cation radical; an intermediate acyl-DCA adduct has been detected and its thermal decomposition to the final product observed. The net result is an unprecendented ketone to amide interconversion in which a strong carbon-carbon bond in the donor is selectively cleaved. Related reactions have been observed with either acceptor and other aminoketones [12].

A series of 1,2-diprimary and ditertiary amines have been found to undergo chemically clean oxidative photofragmentation to yield the corresponding aldehydes, possibly via hydrolysis of the intermediate is in iminimum ions, upon irradiation in the presence of UV or visible light absorbing electron acceptors, e.g. thio-indigo, dicyanoanthracene, tetracyanoanthracene [13].

RESULTS AND DISCUSSION

In the earlier work of Davidson [8] it was shown that UV irradiation of carbonyl [8] and heterocyclic [14] compounds and aromatic hydrocarbons [15] in the presence of 2-(N-aryl)amino-1-phenylethanols results in fragmentation of the alcohols to benzaldehyde and N-arylamines.

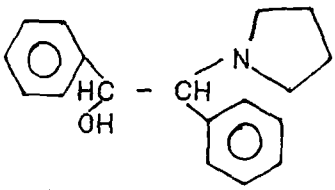
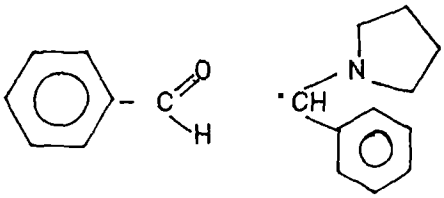
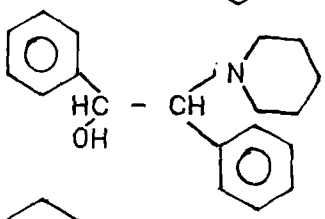
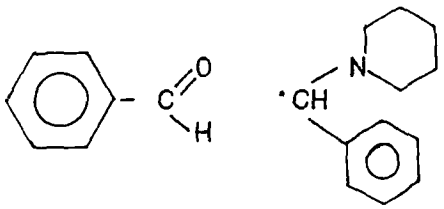
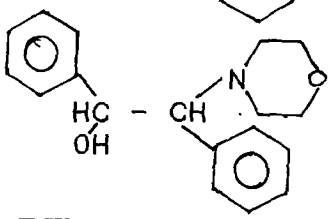
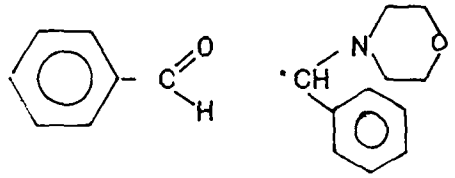
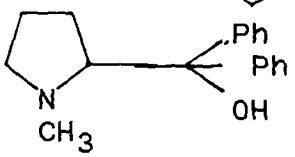
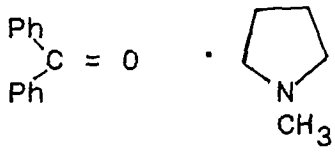
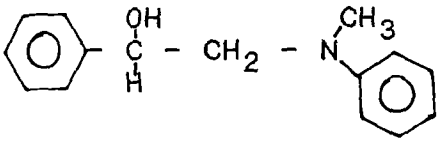
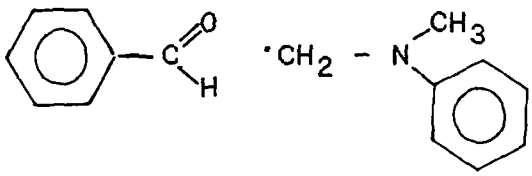
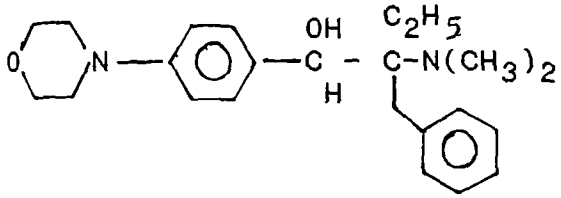
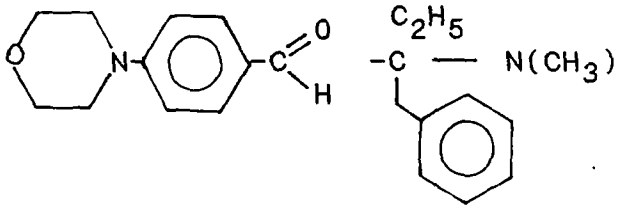
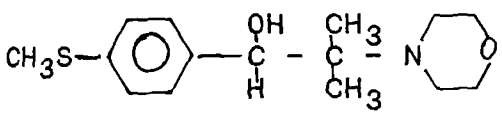
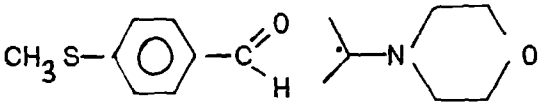
In this study, a series of aminoalcohols were irradiated with acenaphtho[1,2-b]quinoxaline and phenanthro-[9-10-b]quinoxaline using a 350nm fluorescent lamp. The synthesis of aminoalcohols which were used in this study are given in Chapter 2.

The fragmentation of aminoalcohols induced by quinoxalines was examined by irradiating dichloromethane solutions which were 10^{-2}M in quinoxaline and 10^{-2}M in aminoalcohol.

The reactions followed by maintaining the formation of carbonylcompound by glc using naphthalene as an internal standard.

The list of aminoalcohols and expected products after fragmentation in this study are given in Table I.

Table I

Amino Alcohols		Fragmentation Products
	(1)	
	(2)	
	(3)	
	(4)	
	(5)	
	(6)	
	(7)	

The photoproducts derived from the aminoalcohols consist of the carbonyl compound resulting from oxidation of the alcohol concurrent with cleavage of the C-C bond, a secondary amine and a second carbonyl compound (Table I).

Quantitative analysis of the sample is dependent upon the area under each eluting peak. The area has been calculated for an alcohol peak and the products of fragmentation were determined by the difference between the area of alcohol peak before and after photolysis.

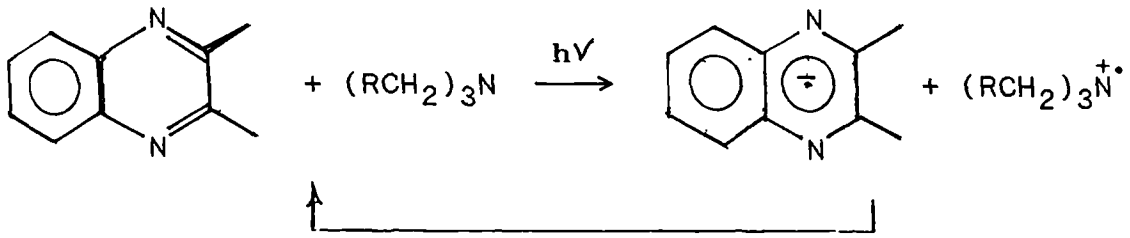
Retention times of carbonyl peaks which were obtained after photolysis of each sample were compared by the injecting of original samples i.e. benzaldehyde, and 4-methylthio benzaldehyde.

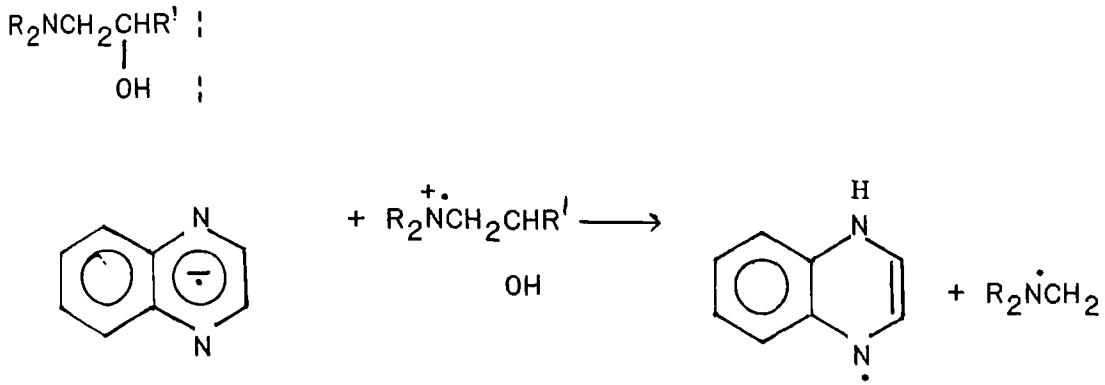
Table

Acceptors	Solvents	Amino Alcohols							
			1	2	3	4	5	6	7
Acenaphtha (1,2-b) Quinoxaline	CH_2Cl_2	Carbonyl Compounds%[a]	75	70	46	40	96	64	55
Phenanthro (9,10-b) Quinoxaline	CH_2Cl_2		70	90	53	51	99	56	64

(a) Yields are based on the amount of amino alcohol

Although the two quinoxalines have different absorption spectra they both exhibit absorption between 300 and 400nm. The reduction potentials of the two compounds are likely to be of similar magnitude since both are quinoxalines and carry similar substitutents. It is therefore expected that the order of reactivity of the various alcohols will be similar for the two quinoxalines. Although quinoxalines are reduced by tertiary amines this process is likely to be less efficient than reaction with 1,2-aminoalcohols since the fragmentation of the latter drives the electron transfer process to the right hand side:





Not surprisingly, as shown in Table II, the most reactive amino alcohol is 5 since the amine is an aromatic amine and the compound readily fragments upon reaction with an excited electron acceptor. The least reactive compound is 4.

Compound 2 appears to be very reactive despite the amino group being a piperidino group. Previous work has shown that piperidines are somewhat more reactive than morpholines. However a factor that will favour the reactivity of (2) is that fragmentation yields in addition to benzaldehyde, an aminoalkyl radical which has additional stabilisation via conjugation with an aromatic group. Compound 6 is interesting since it contains two different amino groups - a morpholine and dimethylamino group. Electron transfer from the latter to the excited quinoxaline can lead to fragmentation to give an α-aminoalkyl radical and an aldehyde which is resonance stabilised by interaction with the morpholino group. A similar situation obtains with 7 where fragmentation produces 4-methylthio-benzaldehyde. Compound 3 has a similar structure to 6 except that the amino group is the less reactive morpholino group. Compound 4 is not as reactive as might have been expected. This compound contains a pyrrolidino group which is known to be a good electron donor. The fact that benzophenone will be produced upon fragmentation should help. However these factors seem to be overshadowed by some other effect. Compound 4 is likely to behave as a sterically

hindered tertiary amine due to the bulky substituent present on the carbon atom at the α-carbon atom of the amine. This steric inhibition will reduce the efficiency of the electron transfer process.

To summarise, the reactivity of the amino alcohols reflects their ability to undergo electron transfer and to fragment to give a resonance stabilised aromatic aldehyde and α-aminoalkyl radical.

EXPERIMENTAL

Materials:

Aminoalcohols and acenaphthoquinoxaline, phenantroquinoxaline were synthesised (Chapter 2). Dichloromethane and naphthalene were obtained from Aldrich.

Irradiation:

$10cm^3$ solutions were irradiated in quartz Pyrex tubes by a circular array of sixteen 8-N block-light fluorescent lamps (350nm Sylvania FT875/BLB) for 24 hours.

The gas liquid chromatography (GLC) experiments were performed on a Perkin Elmer Sigma 3 Chromatograph with a Flame Ionisation Detector using a temperature programme (range 100^{o} for 2 min, to 225^{o} 10^{o} min, 225^{o} 5 min). The separations were performed on a 95% silicon oil column, with nitrogen as the carrier gas.

Personal Acknowledgement

My most sincere thanks to Jeff Abrahams for his help in contributing GLC experiments and the many other things he has done for me.

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CHAPTER 8

AMINOALCOHOLS AND AMINES AS SYNERGISTS

Chapter 8. AMINOALCOHOLS AND AMINES AS PHOTOSYNERGISTS

INTRODUCTION

Amines have two principal uses in UV and visible radiation curing involving radical processes i.e. a photoexcited species reacts with the synergist to produce an amine derived radical which acts as a polymerisation initiator [1,2].

$$A_{So} \xrightarrow{h\nu} A_{S1} \xrightarrow{ISC} A_{T1}$$

$$A_{T1} + (RCH_2)_3N \longrightarrow \dot{A}\text{-}H + (RCH_2)_2\dot{N}CHR$$

$$(RCH_2)_2\dot{N}CHR + \text{Acrylate} \longrightarrow \text{POLYMER}$$

There is plenty of evidence to support the view that ketyl radicals are ineffective initiators of acrylate/methacrylate polymerisation. Other evidence but less direct includes the observation that the rate of initiation of polymerisation is dependent upon the structure of the amino alkyl radical [4].

The second principal use relates to the ability of many tertiary amines to ameliorate the effect of oxygen upon free radical polymerisation processes which leads to poor surface cure [1-5]. The amines act by decreasing the oxygen concentration within the film via a chain reaction as in Fig. 8.1.

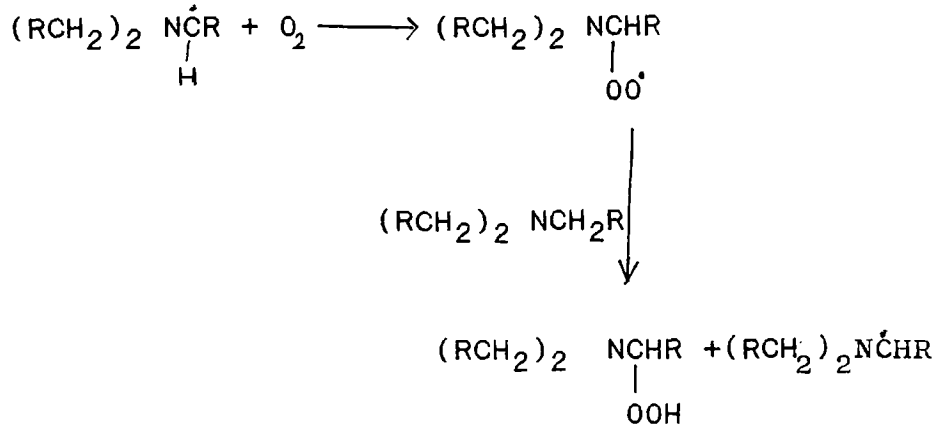


Fig.8.1 Oxygen Scavenging by Amines

Two important facets of this process are that it has to be sufficiently efficient to compete effectively with diffusion of oxygen into the film from the atmosphere and secondly, the products of scavenging oxygen can act as prodegradents thereby reducing the weatherability of the surface coatings produced in this way [6].

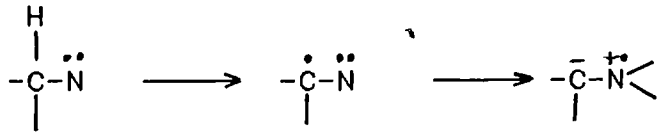
Another process which may be important in UV curing is the reaction of singlet oxygen with tertiary amines. In these reactions the amines act both as physical quenchers of singlet oxygen as well as reacting chemically [7,8].

$$(R_1 - CH_2)_3\ N + {}^1O_2 \longrightarrow (RCH_2)_2\ N\dot{C}HR + H\dot{O}_2$$

It will have been noted that in depleting the oxygen concentration in the film and in quenching and scavenging singlet oxygen, the amine is generating the aminoalkyl

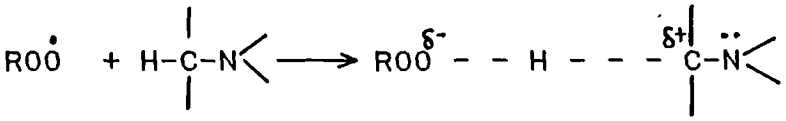
radicals which are polymerisation initiators. This reason brings a very important role to amines in UV curing.

If we consider an aliphatic tertiary amine it can be seen that the lone pair of electrons on the nitrogen can stabilise the incipient radical: This process requires the



overlap of the lone pair orbital with the α-C-H bond which is being broken. The interaction is highly effective unless stereochemical features mitigate against the interaction, and hence the C-H bonds are highly reactive towards radicals.

Electrophilic radicals such as peroxy radicals will be very effective hydrogen abstractors due to the favourable electronic nature of the transition state [9].



These effects are important in the process by which amines enhance surface cure. Aromatic amines can in principle act in a similar way but usually in these compounds the nitrogen lone pair is part of a π-π conjugated system.

Most tertiary amines are characterised by having low ionisation potentials with those of aromatic amines being generally lower than those of aliphatic amines. Due to this property, many amines participate in a plethora of photoinduced electron transfer reactions [10,11,12 and 13]. The electron transfer process may involve orbital interaction between the excited species in the amine to give an exciplex, i.e. an excited complex in which there is some charge transfer between the reaction partners.

$$Sens^* + NR_3 \longrightarrow [Sens^{-} \overset{+\bullet}{N} R_3]^*$$

Exciplex

If the solvent is sufficiently polar the exciplex may dissociate to give free radical ions (solvent separated radical ions) [14].

$$[Sens^{\dot{-}} \overset{+\bullet}{N} R_3]^* \longrightarrow Sens^{\dot{-}}_{solv} + R_3\overset{+\bullet}{N}_{solv}$$

It is also possible for the solvent separated radical ions to be formed via direct electron transfer between the reaction partners [15,16].

$$Sens^* + NR_3 \longrightarrow Sens^{\dot{-}}_{solv} + R_3\overset{+\bullet}{N}_{solv}$$

One of the characteristic features of electron transfer processes is their reversibility i.e. the ease with which reverse electron transfer occurs.

$$Sens^{\cdot-} + R_3N^{+\cdot} \longrightarrow Sens + R_3N$$

In some cases this process leads to the generation of excited states. The back electron transfer can also occur in exciplexes leading to quenching or enhanced intersystem crossing.

Reactions of Carbonyl Compounds with Amines

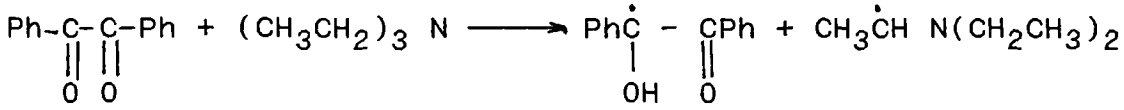
Fundamental work was established by Cohen [17] on aliphatic tertiary amines and by Davidson [18] on aromatic tertiary amines, to show that these compounds are potent reducing agents for carbonyl compounds in their triplet state.

The high efficiency of ISC for most carbonyl compounds and the short lifetimes of the excited singlet states demand that if reaction was to occur via the singlet state, then very high concentrations of amine would have to be used.

These reactions have been reviewed [13], by use of techniques such as flash photolysis [20], esr spectroscopy [21], CIDNP [22] and CIDEP [23]. In many cases, the actual sequence of events i.e. detecting electron transfer, followed by proton

transfer has proved to be difficult to elucidate.

Tertiary amines are able to reduce the excited states of a wide variety of ketones. Due to the electronic absorption properties of thioxanthone (absorption range of 250-400nm) and its derivatives are very important in the UV curing industry and they can be used as sensitisers in pigmented films [24]. Benzil is a low cost carbonyl compound which itself is unreactive, but is photoreduced by tertiary amines [25,26] with the use of polyamines also being claimed as advantageous [27].



Substituted benzils have also been used to advantage [28]. Another important ketone is Michler's ketone 4,4'-di(dimethylamino)-benzophenone [29]. This acts as the sensitiser and as the synergist and consequently does not require the addition of an amine synergist.

α-Ketophosphonates [30,31] have been claimed to be useful in the curing of acrylated unsaturated polyesters. An attractive feature of these compounds is their relatively strong absorption between 300-400nm. Although chalcones and related compounds are known to be photoreduced by amines, this

system does not seem to have been applied to UV curing [32]. For all these reactions, the excited carbonyl compound interacts with the amine to generate an amine derived radical which can escape the solvent cage and then initiate polymerisation. The efficiency of the primary reaction is governed by the energetics of electron transfer, the concentration of the amine employed and the viscosity of the medium. Systems where the amine will participate in hydrogen bonding may well be less reactive due to the bonding increasing the energy required to ionise the lone pair.

The rate constants for reaction of many carbonyl compounds with a variety of amines have been tabulated [10].

Effect of Amine Structures

Acidity of α-CH bonds

It has been found that there is a correlation between the acidity of the α-C-H bonds and the ability of an amine to act as a synergist. N-methylamines are found to be more reactive than their N-ethyl counterparts [33] although in a study of some NN-dialkylaminoethyl methacrylates the N-ethyl compounds were found to perform better than their N-methyl counterparts [34]. It has been shown that for N-methyl compounds electron transfer is usually rapidly followed by proton transfer to give the desired radical.

e.g. $R_2NCH_3 \longrightarrow R_2\dot{N}CH_2$ [35]

$R = HOCH_2CH_2$

$PhN(CH_3)_2 \longrightarrow Ph\text{-}N(\cdot CH_2)\text{-}CH_3$ [23 and 36]

These radicals are potent reducing agents and may reduce a ground state carbonyl compound [19].

$R_2NCH_2CH_3 \longrightarrow R_2N\dot{C}HCH_3 \longrightarrow$ Initiation

$R_2N\dot{C}HCH_3 \longrightarrow R_2NCH=CH_2$ (Enamine)

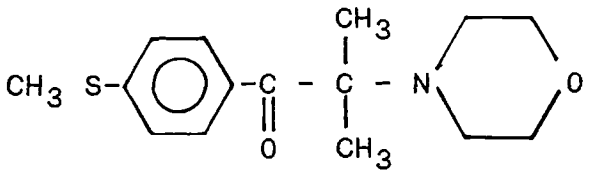
Enamines are formed as products in the photoreduction of carbonyl compounds by tri-n-alkyl amines. It is also possible that this type of radical will facilitate amines acting as chain transfer agents thereby affecting the properties of the surface coating [32].

This type of reaction can also dominate the ability of an amine to act as an ameliorator of oxygen inhibition.

Secondary alkyl groups (e.g. 2-propyl) attached to nitrogen produce a relatively hindered amine. This situation is also

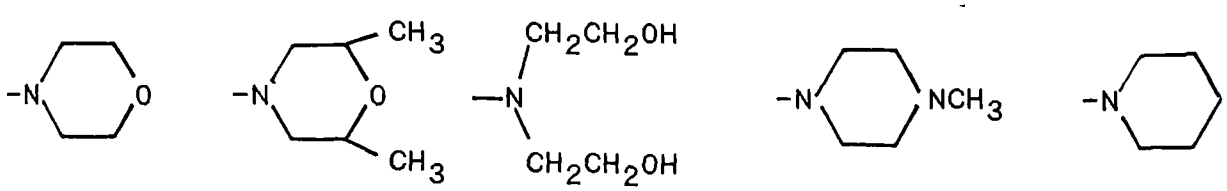
true for N-alkyl derivatives of piperidine. It has also been shown that the steric hinderance exhibited by such compounds and related species reduced the rate constant for excited complex formation [37]. An N-2-propylamine is expected to quench excited states less efficiently than triethylamine and probably back electron transfer will occur in preference to the sterically demanding proton transfer step. N-t-butylamines cannot undergo α-C-H bond cleavage from the t-butyl group but they may act as quenchers of excited states.

These issues come to the fore when one considers the recently introduced photoinitiator which carries a morpholino substituent [38].



Despite this compound having a $\Pi\Pi^*$ triplet it undergoes the Norrish Type I reaction. Of all amine groups studied the morpholino was found to be the most reactive.

Relative reactivity respectively:



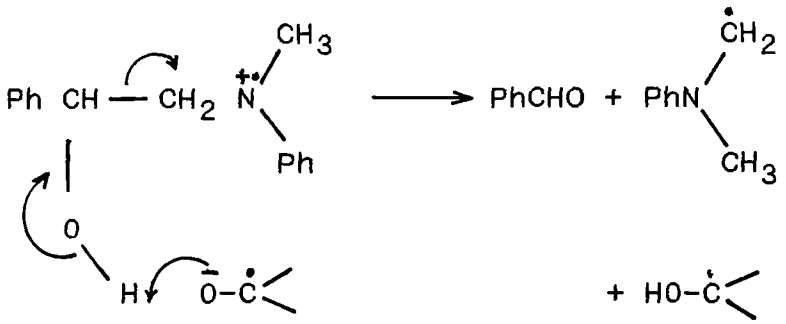
130 80 80 70 60

These effects are not easily rationalised but may possibly reflect the ability of the amine to stabilise the incipient radical.

AMINOALCOHOLS AS SYNERGISTS

The ethanolamines were found to be excellent synergists despite their relatively low efficiency in quenching the excited states of ketones [24]. As yet there has been no satisfactory explanation for this phenomenon.

A special feature of many of the 2-aminoalcohols is that following oxidation they undergo fragmentation.



This fragmentation can drive the electron transfer reaction in the desired direction. These reactions have been developed further in a study of electron transfer reactions [39,40]. The key to the fragmentation process is to provide a hydrogen more acidic than the α-C-H groups and to provide a fragmentation pathway that will produce a stable species.

RESULTS AND DISCUSSION

A wide range of aminoalcohols was synthesised as has been mentioned in Chapter 2 and they were used as synergists in the polymerisation of a number of acrylates using different methods. Many of them exhibited poor solubility in the acrylates thereby limiting their usefulness.

Some of these solid aminoalcohols and initiators were dissolved in chloroform and then a certain amount of these mixtures was added to trimethylolpropanetriacrylate (TMPTA). This method was found to be very inefficient in testing the synergistic effect of aminoalcohols in films.

Benzophenone was used as an initiator with these aminoalcohols. The polymerisation was achieved using Fusion Color Dry System with a 300W/per inch medium pressure mercury lamp. The same dose of radiation was given to each sample. Curing in thin film was determined by Pendulum Hardness. Cure was assessed from Pendulum Hardness measurements as those shown in Fig 8.2.

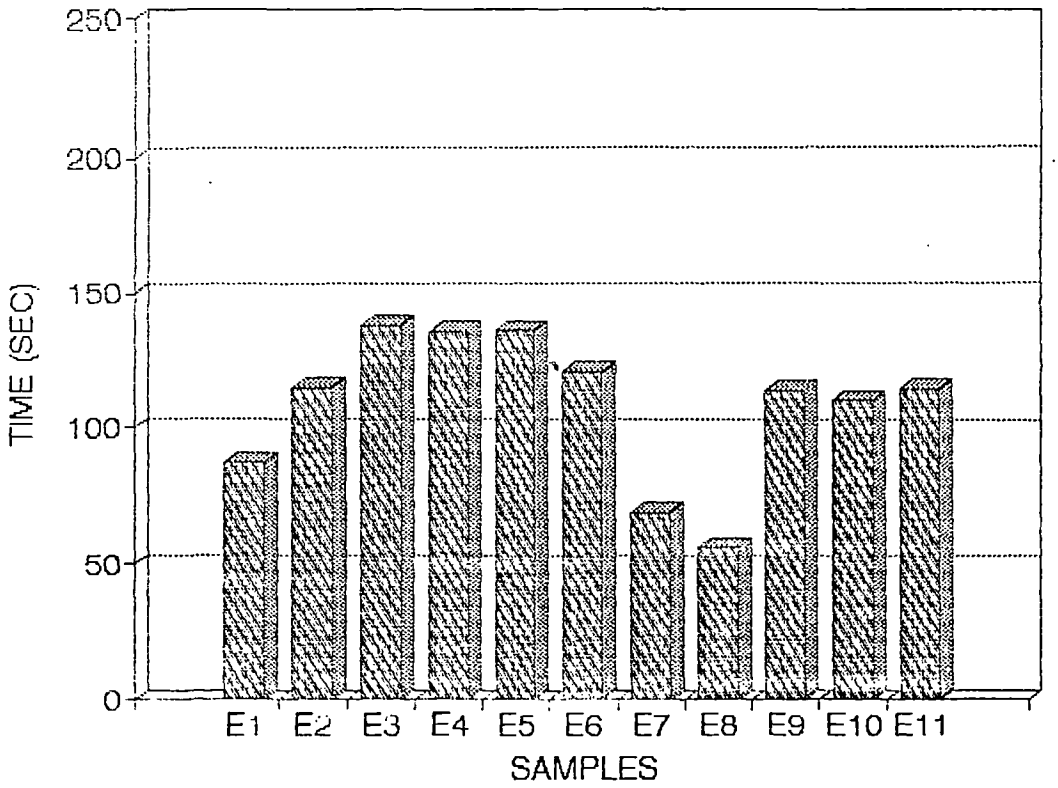


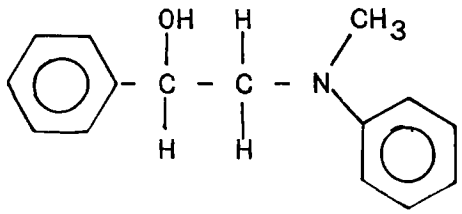
Fig 8.2 Pendulum Hardness Results (sec) of Samples E1 - E11

The list of aminoalcohols is given in Table 9.1 , page 251(a)As can be readily seen the E1 sample which consisted of NMDEA/BP gave a film having a lower damping time than other aminoalcohols.

Samples E3, E4 and E5 had a much higher damping time than E1, and this result indicates a far more effective cure.

Curing in these films was also assessed by infrared spectroscopy. FTIR spectroscopy was used to measure the residual unsaturation in these films. More detailed information about FTIR spectroscopy is given in Chapter 1 .

2-(N-Methyl-N-phenylamino)-1-phenyl ethanol (1) (MPAPE):



(1)

was chosen due to its good solubility in reactive diluents. Its efficiency as a synergist and oxygen scavenger was tested using different types of initiators mainly, Irg-907 (Type I) and ITX (Type II) in different commercial acrylates e.g. Sartomer 259 (Polyethyleneglycol (200) Diacrylate Sartomer 344 (Polyethyleneglycol (400) Diacrylate), Photomer 4094

(Aliphatic trifunctional acrylate, Viscosity 100 cps/25^{o}C), Photomer 4194 (Aliphatic trifunctional acrylate, Viscosity 70-85 cps/25^{o}C). The results are recorded as the percentage of residual double bonds remaining after UV irradiation.

As can be clearly seen from Fig 8.3 the residual unsaturation dropped very quickly after only one pass. Aminoalcohol (MPAPE) with Irg-907 in P.4094 showed the best performance. The residual unsaturation dropped to 12%. After ten passes, the residual unsaturation of all the samples nearly disappeared, the value was 2% for AX4 (ITX/MPAPE/ P.4094).

AX5 : 2%ITX/1% $PhCHOHCH_2NMePh$/S.344

AXP4 : 2%ITX/1% $PhCHOHCH_2NMePh$/P.4094

AIP4 : 2%Irg-907/1% $PhCHOHCH_2NMePh$/P.4094

AIP9 : 2%Irg-907/1% $PhCHOHCH_2NMePh$/P.4149

AA1 : 2%Irg-907/1% $PhCHOHCH_2NMePh$/TMPTA

AA2 : 2%ITX/1% $PhCHOHCH_2NMePh$/TMPTA

NMI1 : 2%Irg-907/10% NMDEA/TMPTA

NM12 : 2%ITX/10% NMDEA/TMPTA

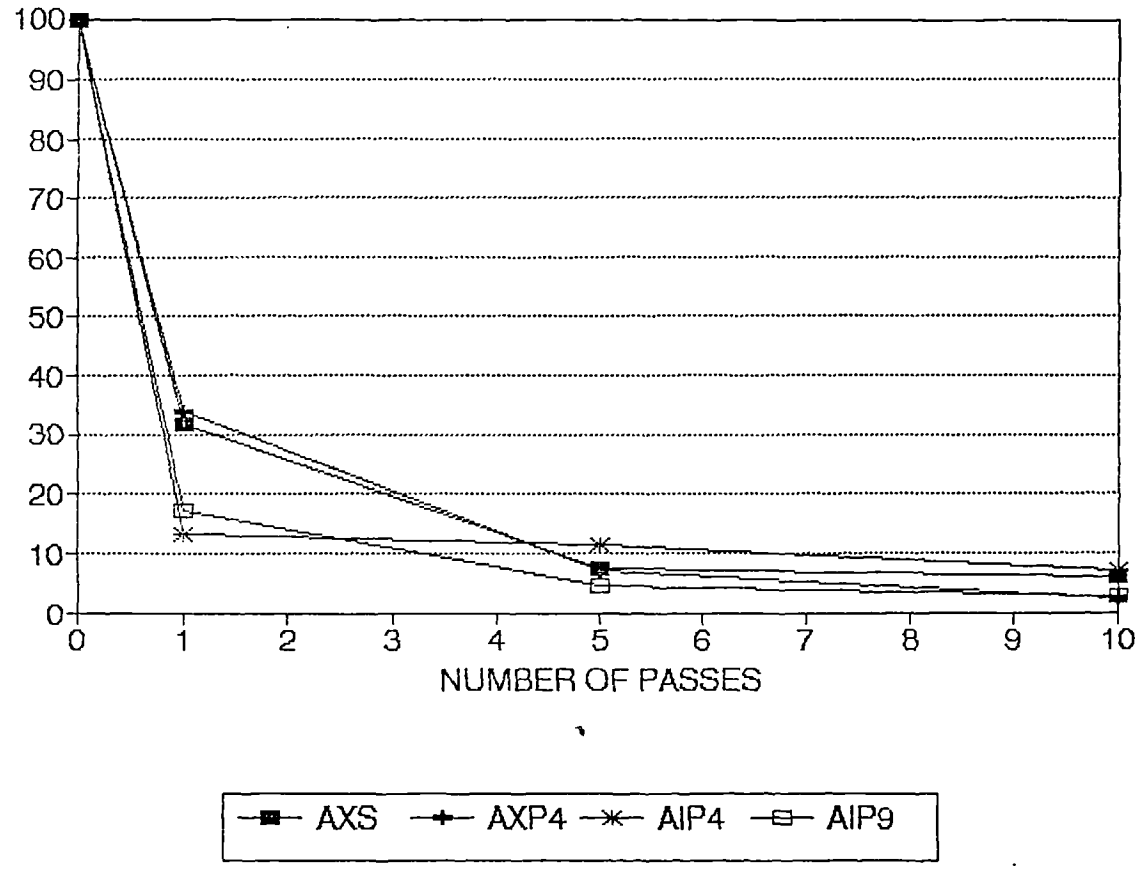


Fig 8.3 The residual unsaturation of samples (AXS, AXP4, AIP4 and AIP9) determined using FTIR

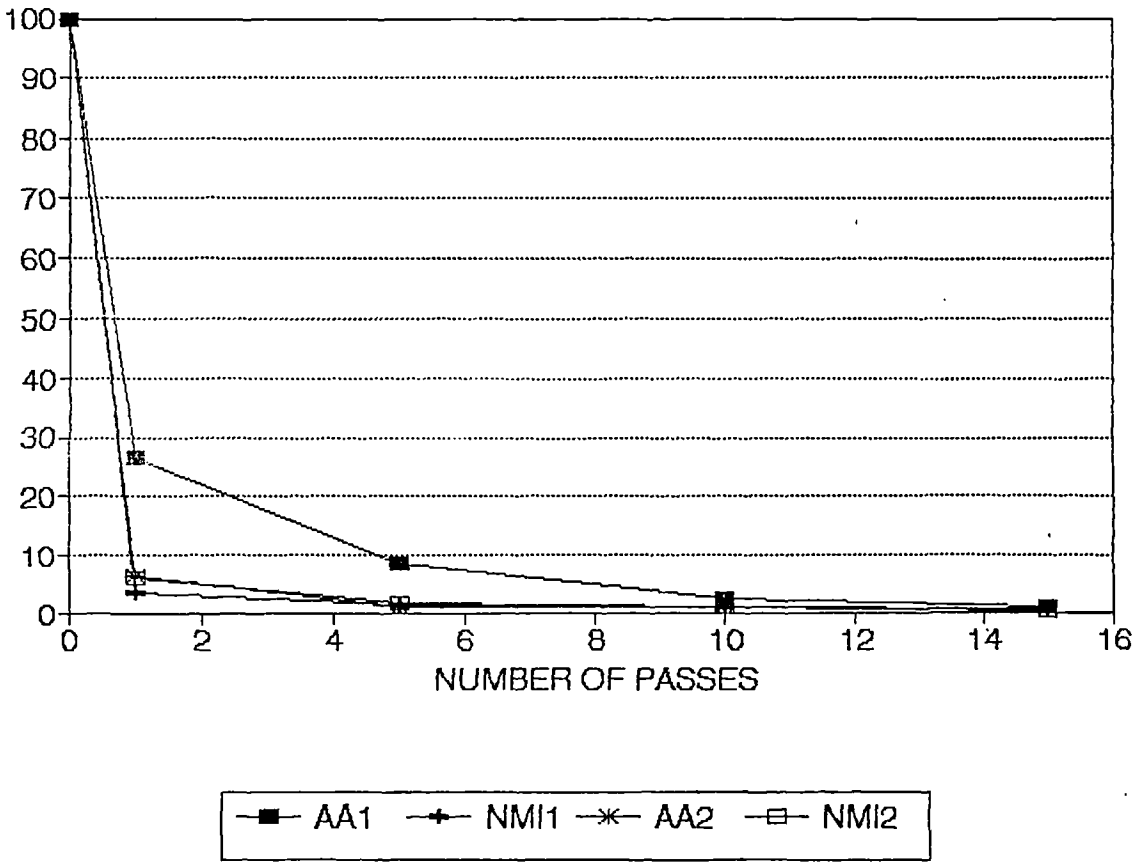


Fig 8.4 The residual unsaturation of samples (AA1, NMI1, AA2 AND NMI2) determined using FTIR

Although the aminoalcohol concentration (MPAPE) was very low, the synergistic effect of aminoalcohol was as efficient as NMDEA in the case of ITX (Fig.8.4).

This effect of amines can be attributed to the known ability of amines to act as efficient oxygen scavengers [12,14,15,16,17,18, Irg-907/ITX].

Aminoalcohol (MPAPE) was also compared with NMDEA in TMPTA using Colordry. The results are given in Figs.8.5 and 6 for cure in air and in Figs.8.7 and 8 for curing using a glass filter.

From the results for cure in air, NMDEA was found to be more efficient than aminoalcohol (MPAPE) when Irg-907 was used as a photoinitiator in the same concentration of ITX. NMDEA was slightly better than aminoalcohol (MPAPE). The changing of aminoalcohol concentration in the case of ITX changed the rate of cure.

A similar result was obtained when benzophenone (BP) was used as a photoinitiator for cure in air and using a glass filter as shown in Figs.8.6 and 8 respectively.

YO : 2% Irg-907/TMPTA

Y1 : 2% Irg-907/10% NMDEA/TMPTA

Y2 : 2% Irg-907/10% $PhCHOHCH_2NMePh$/TMPTA

Y3 : 2% ITX/10% NMDEA/TMPTA

Y4 : 2% ITX/10% $PhCHOHCH_2NMePh$/TMPTA

Y5 : 2% ITX/1 % $PhCHOHCH_2NMePh$/TMPTA

Y6 : 2% Irg-907/1% $PhCHOHCH_2NMePh$/TMPTA

Y7 : 2% BP/1% $PhCHOHCH_2NMePh$/TMPTA

Y8 : 2% BP/10% $PhCHOHCH_2NMePh$/TMPTA

C1 : 2% Irg-907/1% $PhCHOHCH_2NMePh$/S-259

C2 : 2% Irg-907/1% $PhCHOHCH_2NMePh$/S-344

C3 : 2% Irg-907/1% $PhCHOHCH_2NMePh$/TMPTA

C4 : 2% Irg-907/1% $PhCHOHCH_2NMePh$/P.4149

C5 : 2% Irg-907/1% $PhCHOHCH_2NMePh$/P.4094

C6 : 2% ITX/1% $PhCHOHCH_2NMePh$/S.344

C7 : 2% ITX/1% $PhCHOHCH_2NMePh$/TMPTA

C8 : 2% ITX/1% $PhCHOHCH_2NMePh$/P.4149

C9 : 2% ITX/1% $PhCHOHCH_2NMePh$/P.4094

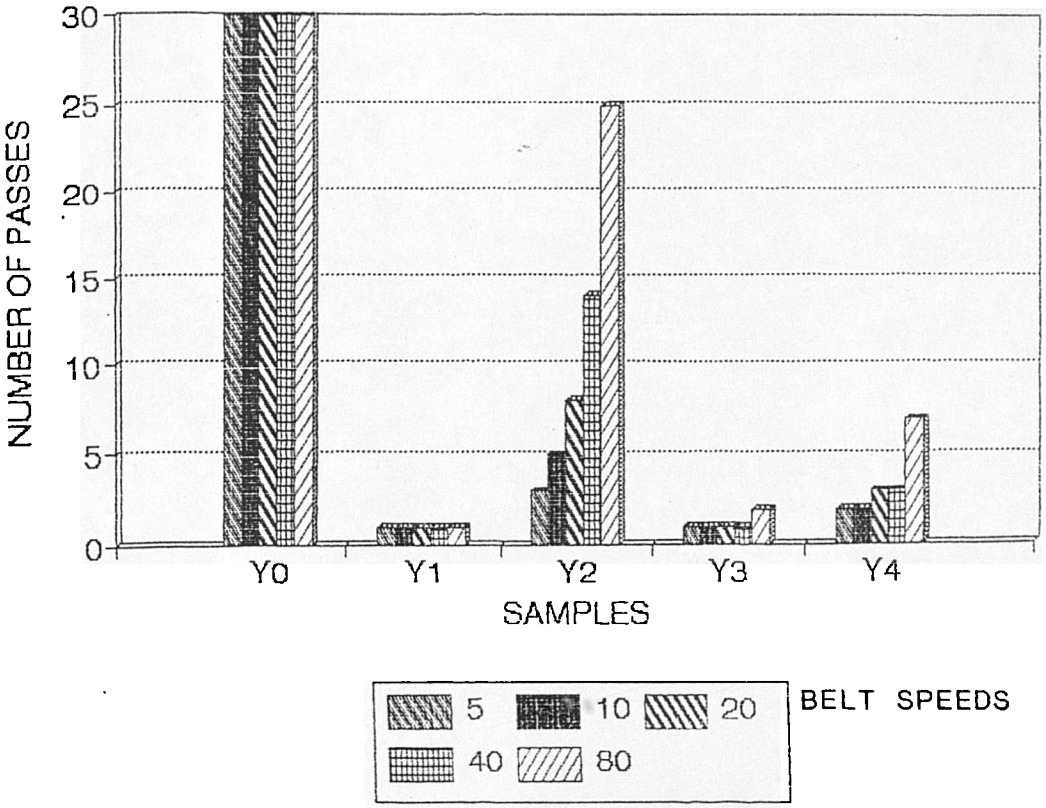


Fig.5 The curing results of samples (Y0-Y4)

in air using Colordry

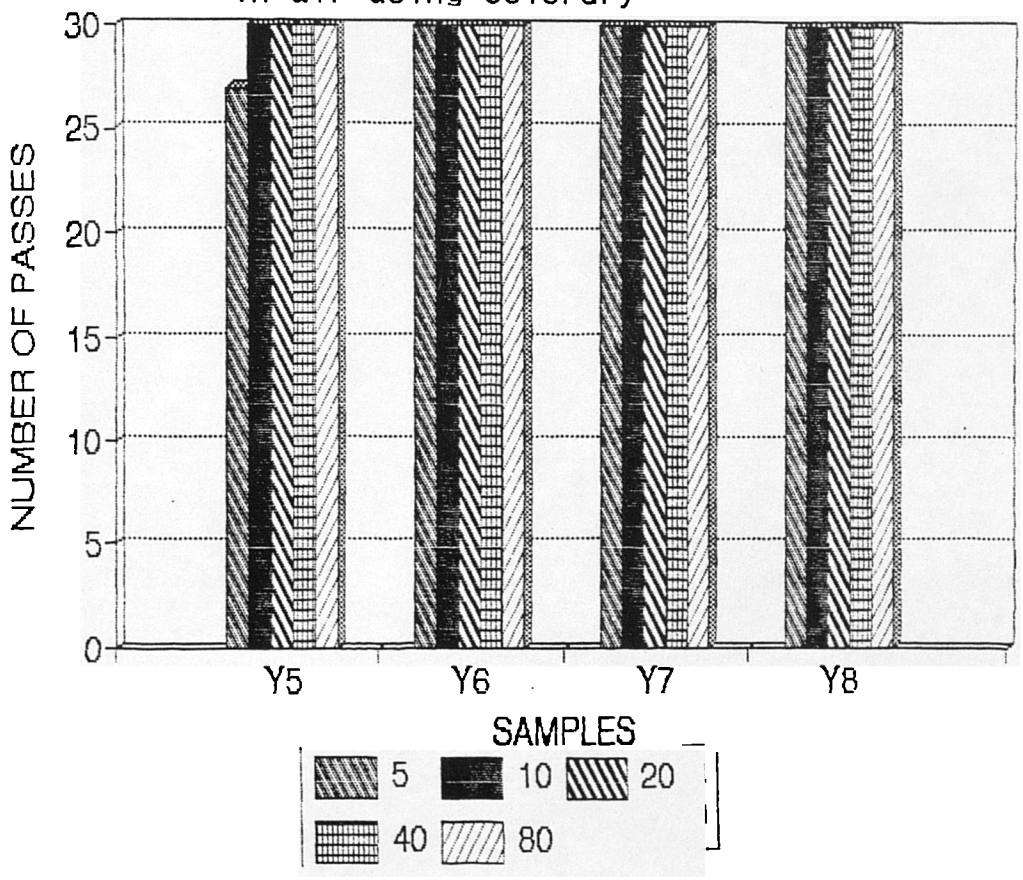


Fig 8.6 The curing results of samples (Y5-Y8)

in air using Colordry

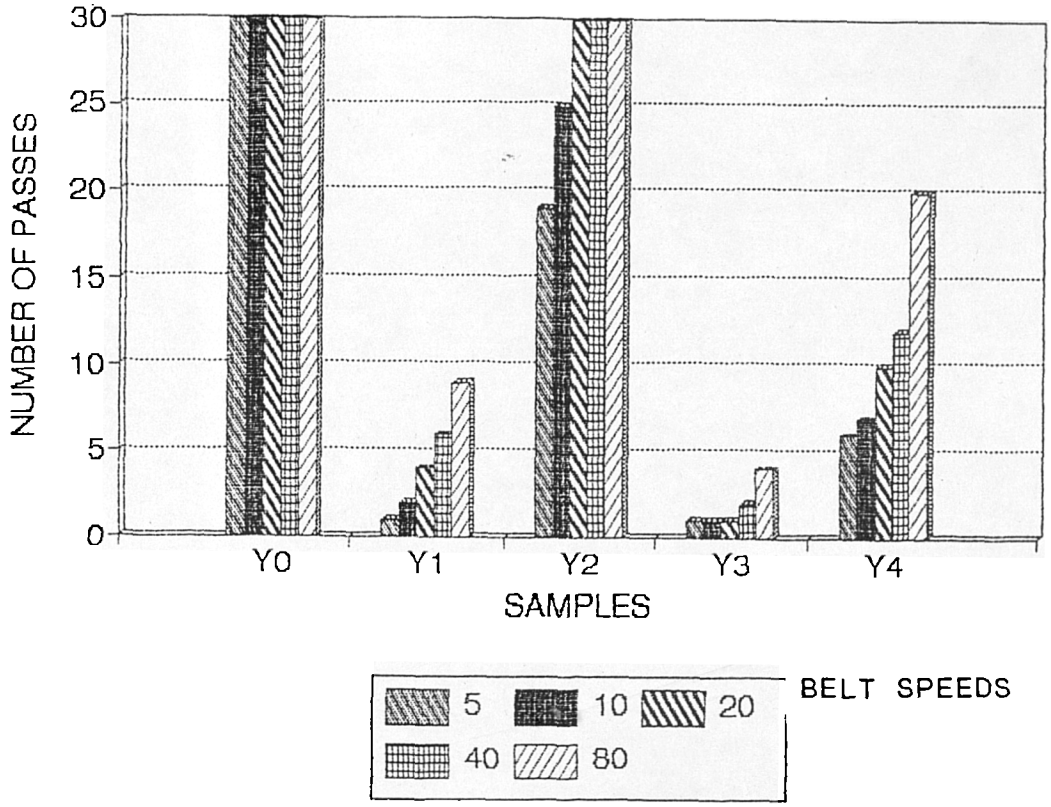


Fig 8.7 The curing results of samples (Y0-Y4) using a glass filter

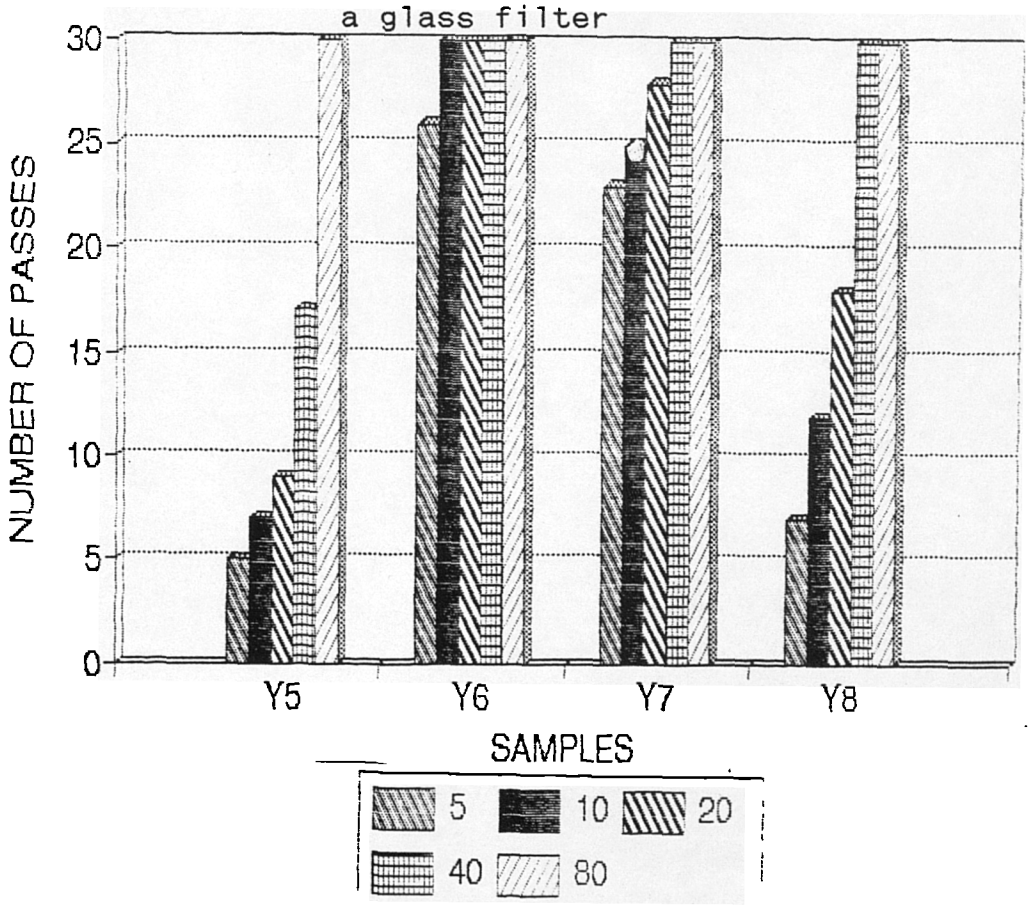


Fig 8.8 The curing results of samples (Y5-Y8) using a glass filter

IR + Colordry Results

The percentage of acrylate groups converted was obtained using IR spectrophotometry for samples cured using Colordry Solutions of different acrylates containing the same amount of aminoalcohol (MPAPE) were made up with half containing Irg-907 as initiator and the other half containing ITX. Films of the samples were irradiated using the Colordry and the extent of acrylate groups converted determined by IR spectroscopy.

From these results, the samples either with Irg-907 or ITX in trimethylolpropanetriacrylate (TMPTA) gave less conversion percentage compared to the other acrylates. Very high conversions were obtained for the polyethyleneglycol-diacrylates which reflects the mobility of the polyether chain. The factors to increased mobility also result in a slower increase in viscosity during cure than is found with TMPTA.

The triacrylates which have polyether components also cure efficiently but due to the higher functionality, the rise in viscosity on cure is more rapid than for the diacrylate and consequently some acrylate groups become "frozen out".

Irg-907 in combination with the aminoalcohol at the 1% level leads to extensive cure of a number of diluents. The polyethyleneglycol diacrylates lead to the greatest number of

acrylate double bonds being used. The triacrylate containing polyether residues cure to ~60% very quickly and then much more slowly. This presumably reflects the rapid increase in viscosity due to crosslinking. After 60% of the double bonds have been used cure is very slow. TMPTA will produce a coating having a much higher crosslink density than any of the other materials and this is reflected by the consumption of only 40% of the double bonds after one pass (Fig.8.9)

With ITX and the aminoalcohol at the 1% level the polyetheneglycol diacrylate can be freely cured but the rate of cure is rather slow. This result parallels that obtained with Irg-907. Given that ITX absorbs more of the incident radiation of the Irg-907, the ITX curing is remarkably slow. Since it initiates from a biomolecular process, it will be far more sensitive to viscosity increases than a Type I initiator (Fig.8.10).

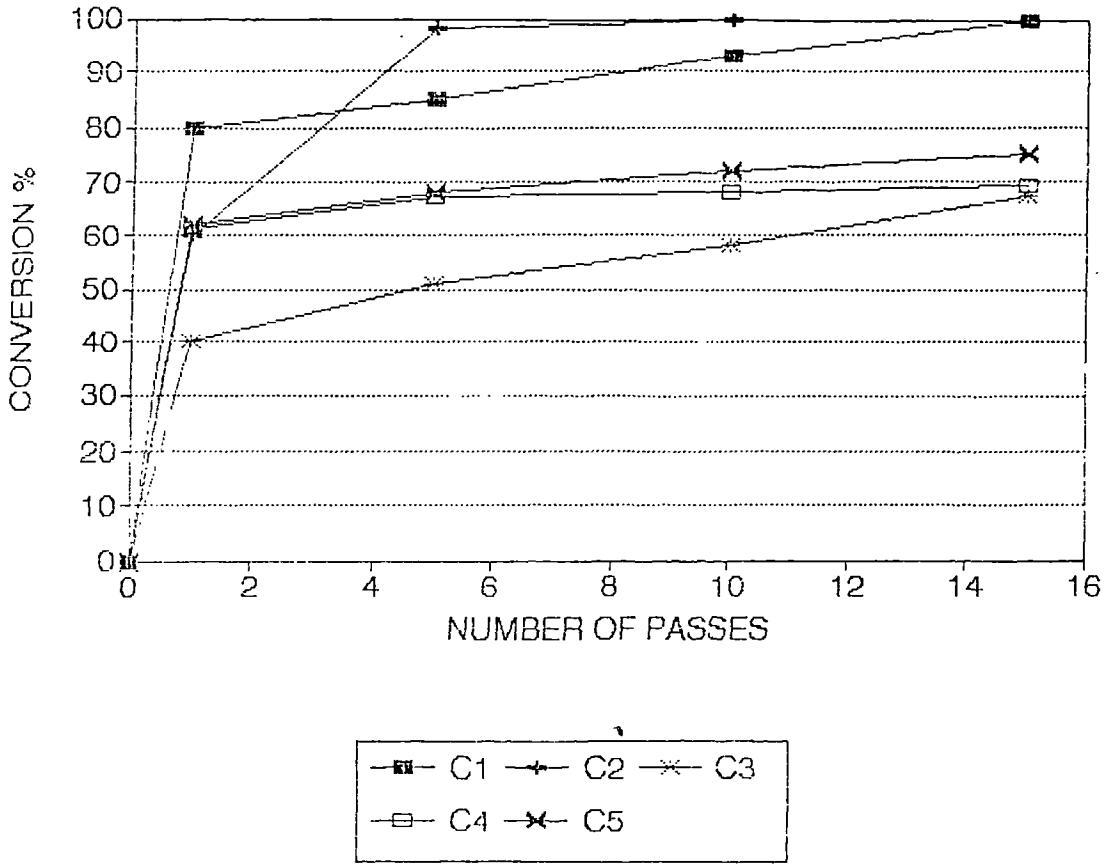


Fig 8.9 The Conversion% of Samples (C1-C5) using RTIR

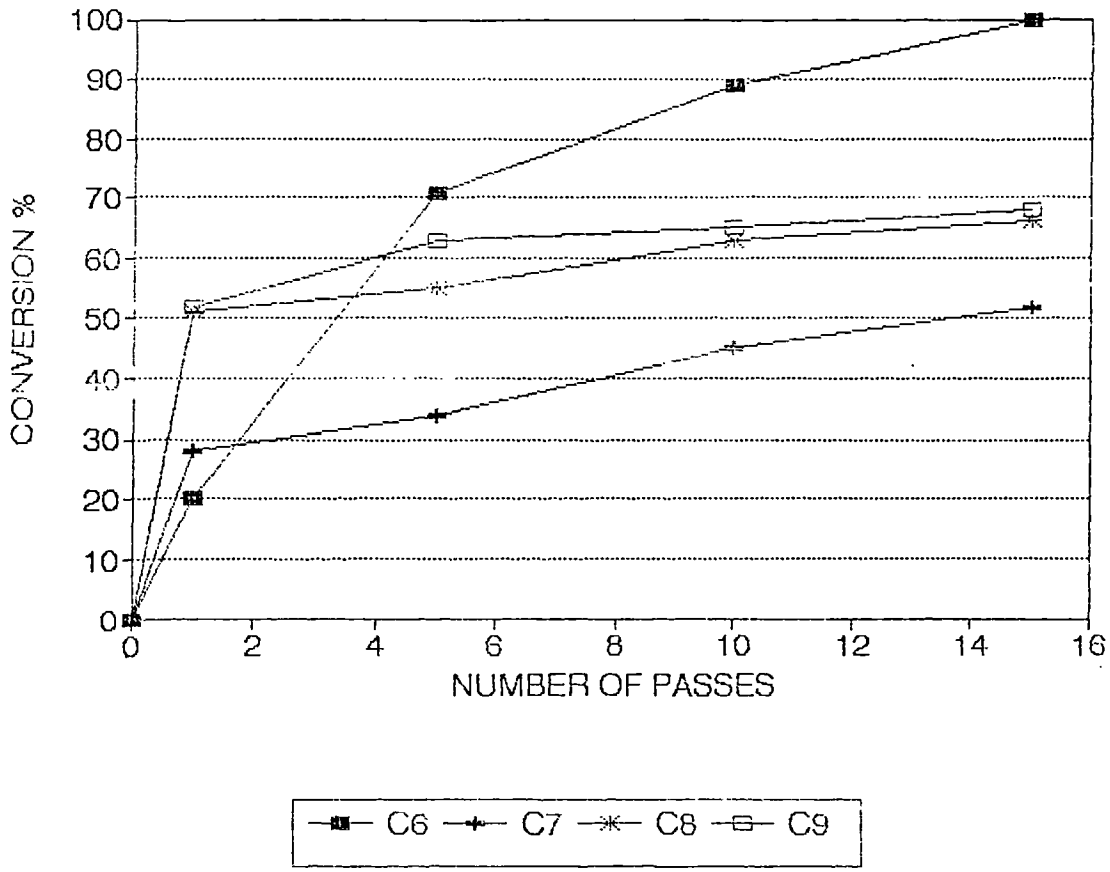


Fig 8.10 The Conversion% of Samples (C6-C9) using RTIR

AIR 1 : 0.005g Irg-907/0.0227g AA

AIR 2 : 0.01g Irg-907/0.0227g AA

AIR 3 : 0.02g Irg-907/0.0227g AA

X1 : 0.005g ITX/0.0227g AA

X2 : 0.01g ITX/0.0227g AA

X3 : 0.02g ITX/0.0227g AA

Not surprisingly, the weight of polymer formed increases as the initiator concentrate increases.

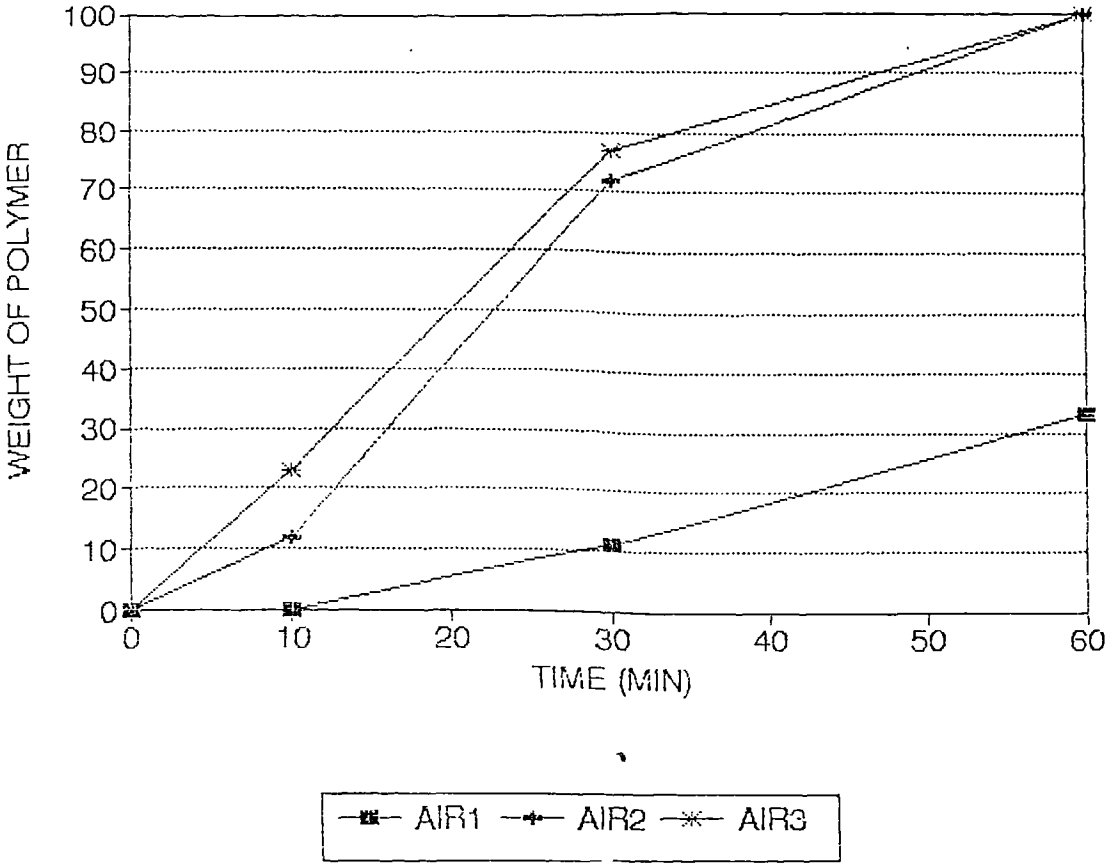


Fig 8.11 The Bulk Polymerisation Results of Samples (AIR1, AIR2 and AIR3)

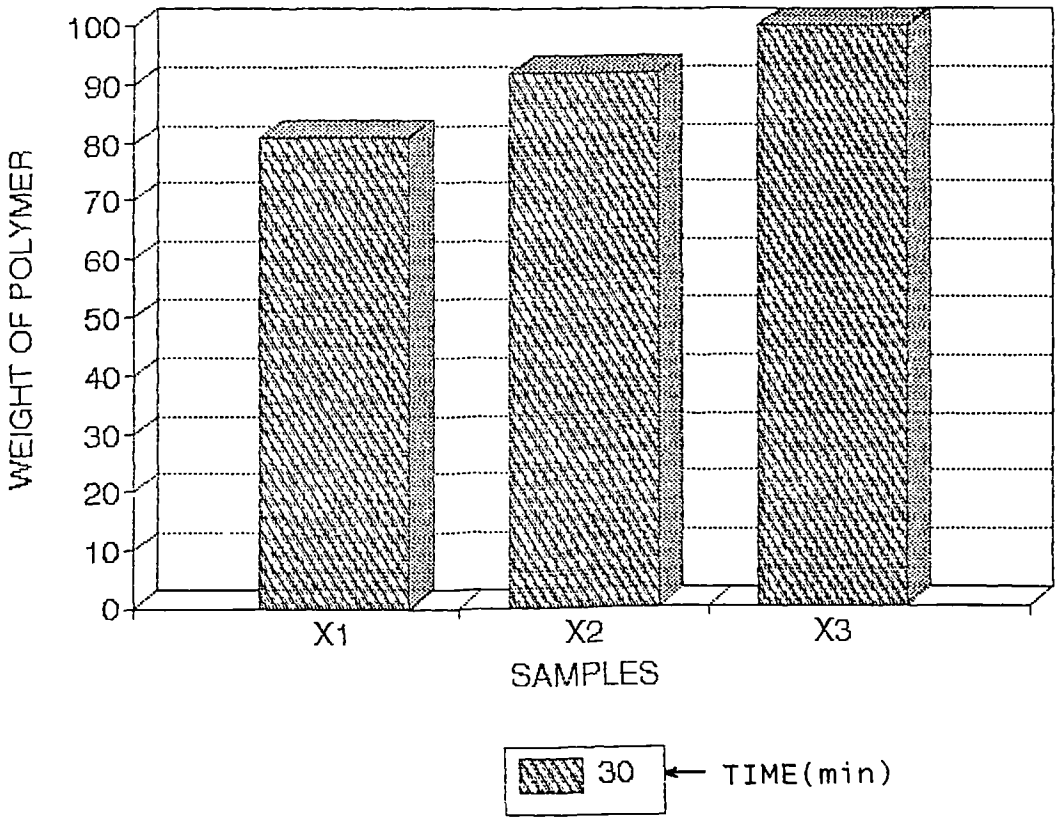


Fig 8.12 The Bulk Polymerisation Results of Samples (X1, X2 and X3)

In the bulk polymerisation reactions the initiator concentration was changed while the aminoalcohol concentration was held constant for different irradiation times. More information about bulk polymerisation Technique is given in Chapter 3.

Trimethylolpropanetriacrylate was used as the acrylate. As the concentration of initiator was increased so the weight of polymer produced is also increased. As can be seen from Figs.11 and 12 for Irg-907 and ITX respectively.

The samples X1, X2 and X3 were irradiated for 30 min and AIR1, AIR2 and AIR3 were irradated for a set period of time. In this case, increasing the concentration of initiator led to more initiating radicals being produced per unit of time.

It was found that these aminoalcohols can be used as an initiator as well as a synergist. The aminoalcohols: 2-(N-Methyl-N-Phenyl-amino)-1-phenyl ethanol, 2-Methyl-1-[4-(methylthio)phenyl-2 morpholino-propane-1-ol and 2-benzyl-2-dimethyl-amino-1-(4-morpholinophenyl)-butan-1-ol were tested in the presence of NMDEA in trimethylolpropane triacrylate using the Colordry curing system. All these results were compared with the sample consisting of Irg-907 in the presence of NMDEA (M1). The results of cure in air, using a glass filter, glass coverslip and quartz coverslip are given in Figs.8.13, 14, 15 and 16, respectively.

Fig.8.13 shows the polymerisation of TMPTA initiated by Irg-907 requires the presence of an amine synergist. In the presence of NMDEA cure is relatively efficient and this is probably due to the amine acting as a synergist as well as reducing the effect of O_2 inhibition. The use of aromatic aminoalcohols introduces another factor - namely the aminoalcohol competes with the Irg-907 for some of the incident radiation. The aminoalcohol derived from Irg-369 (2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-butan-1-ol (M3) has two amino groups. The morpholino group can act as an electron and proton donor but will be less effective than the dimethylamino group. This latter group can act as an electron and proton donor and also lead to fragmentation of the aminoalcohol. 2-Methyl-1-[4-(methylthio)[-phenyl-2-morpholinopropane-1-ol has only a

morpholine group but if it acts as a donor, it may serve to trigger fragmentation. The methylthio group may well act as a physical quencher. Disappointingly, 2-(N-Methyl-N-phenylamino)1-phenylethanol proved to be the least effective aminoalcohol. This could be the clue as to what is influencing reactivity. α - Cleavage of this aminoalcohol gives benzaldehyde which is less stable than 4-Methylthio benzaldehyde which in turn is less stable than 4-morpholino benzaldehyde. Thus the reactivity of the aromatic aminoalcohols appear to be governed by the stability of the aldehyde molecule on fragmentation.

Fig.8.14 shows placing a glass filter between the light source and the film reduces the curing efficiency in a dramatic way and shows clearly that the most effective aromatic alcohol is the one which fragments to give the most stable aromatic aldehyde.

M1: 1% Irg-907/ 10% NMDEA/ TMPTA

M2: 1% Irgacurol/ 10% NMDEA/ TMPTA

M3: 1% Morpholinol/ 10% NMDEA/ TMPTA

M4: 1% PhCHOHCHNCHPh/ 10% NMDEA/TMPTA

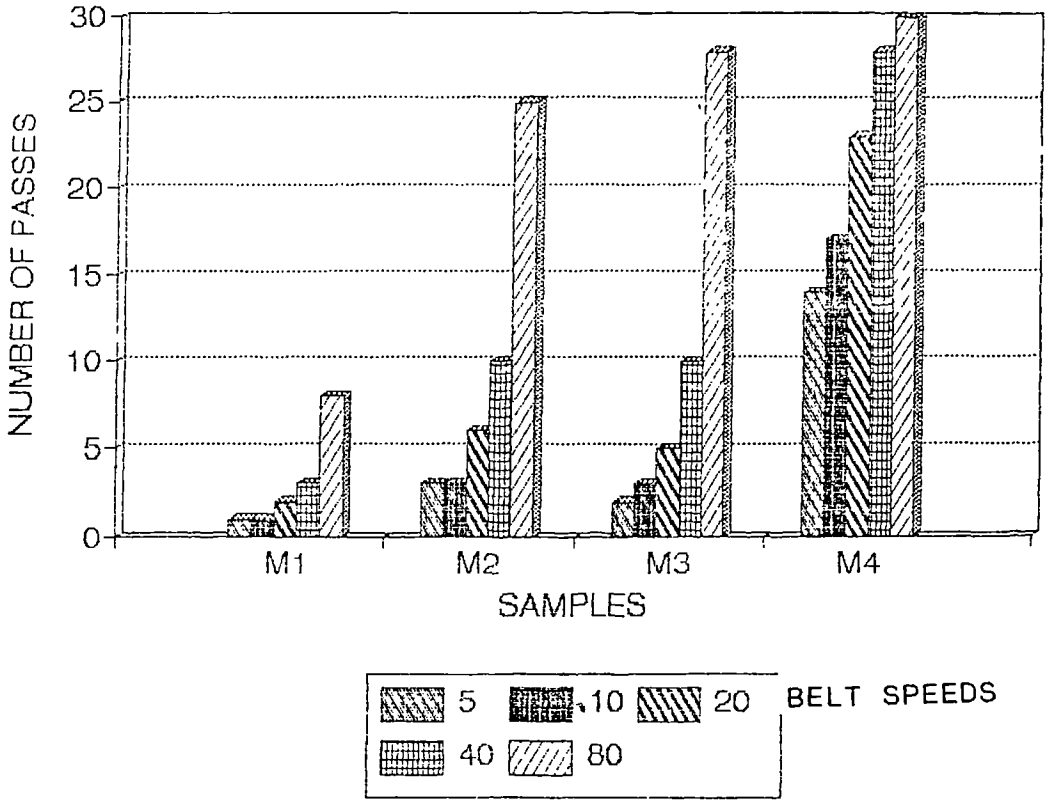


Fig 8.13 The curing results of Samples (M1-M4) in air using Colordry

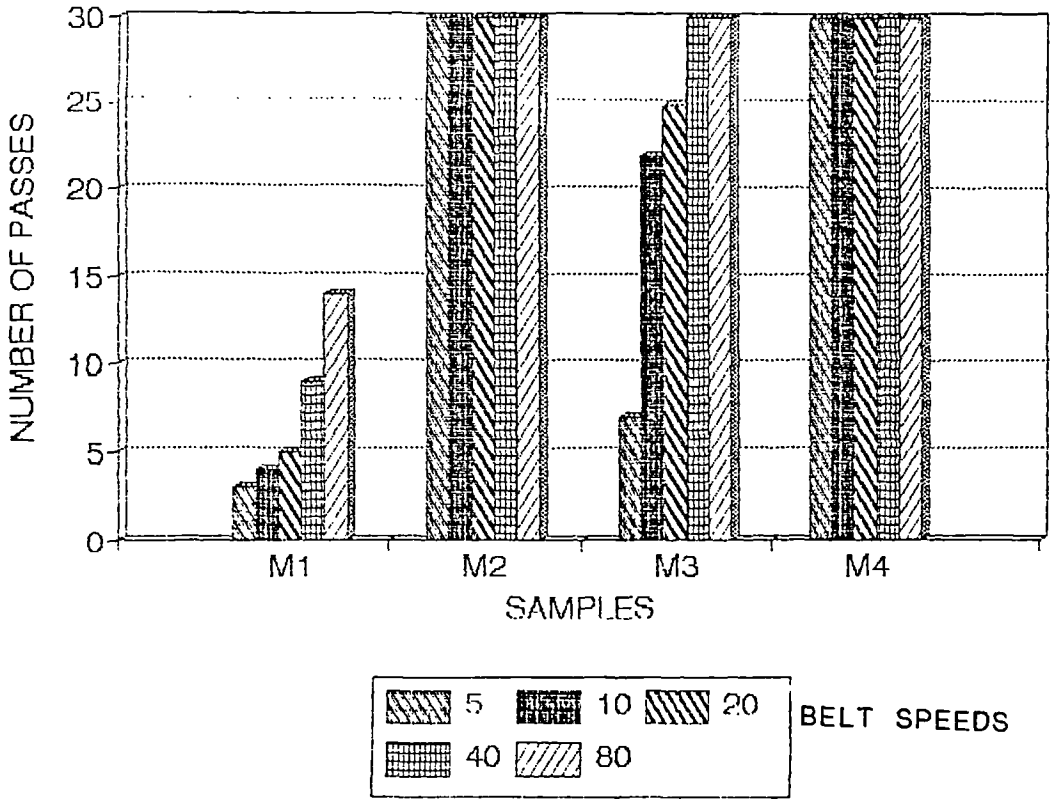


Fig 8.14 The curing results of Samples (M1-M4) using a glass filter

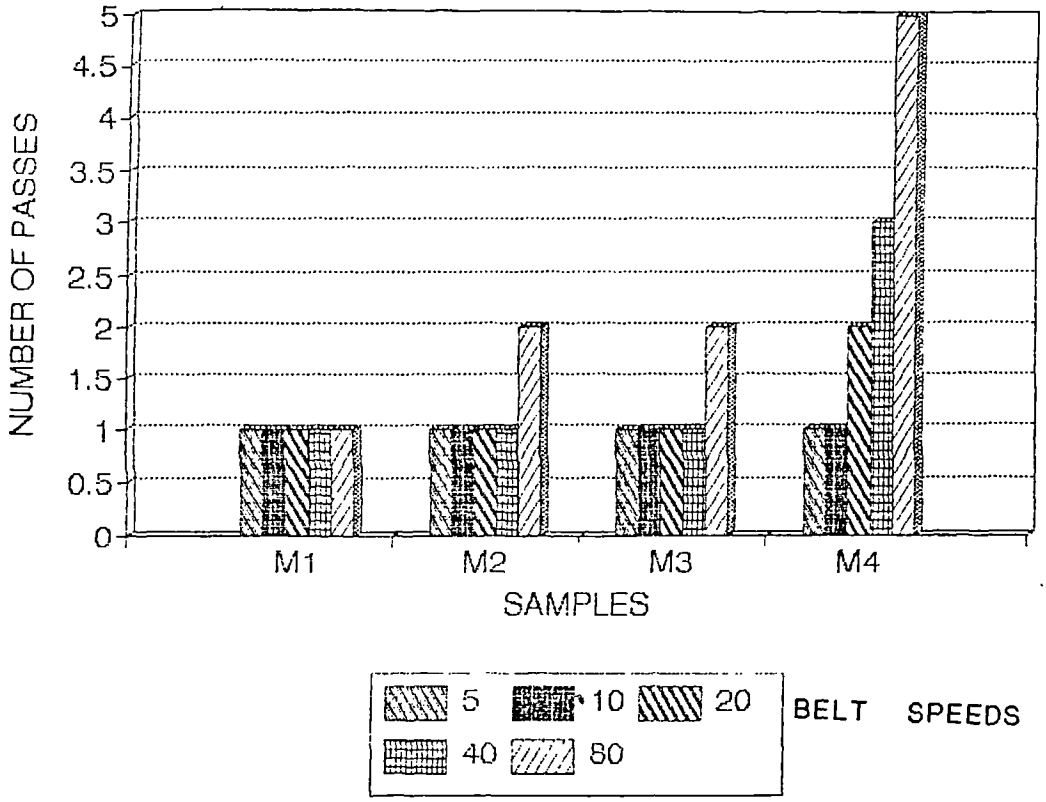


Fig 8.15 The curing results of Samples (M1-M4) using a glass coverslip

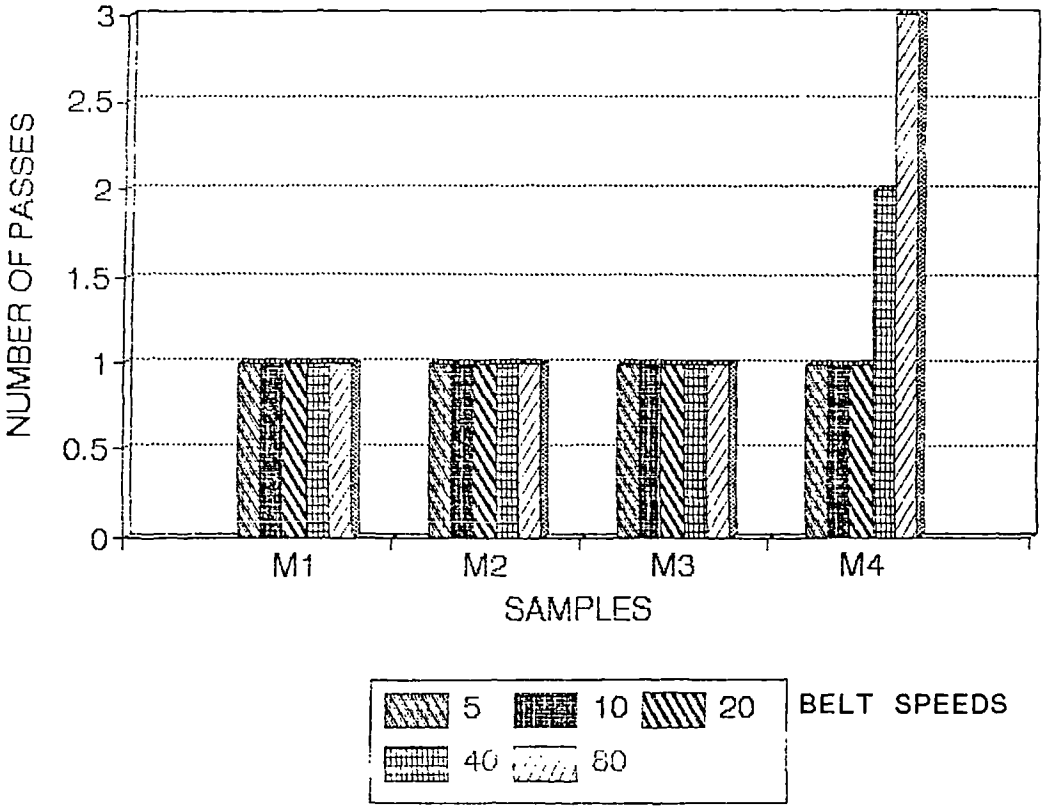


Fig 8.16 The curing results of Samples (M1-M4) using a quartz coverslip

Amines

N-Methyldiethanolamine (NMDEA), N-Methylmorpholine (MM), 1,3-Dimorpholinopropane (DMP), 4-Morpholinoethanol (ME). Isopropylpyrrolidine (IPR) and Isopropylpiperidine (IPP) in TMPTA were tested using IR spectroscopy combined with Colordry. Irg-907 was used as photoinitiator.

The conversion percentage of amines were calculated depending on a number of passes (1 and 5).

One of the, as yet unexplained mysteries, covering the use of amines as synergists is the high reactivity of NMDEA. Previously it has been shown that the closely related 1,3-dimorpholinopropane is a good synergist but as Fig 8.17 shows it is not as good as NMDEA. N-Methylmorpholine is possibly slightly better than the 1,3-dimorpholinopropane and this may reflect the greater number of C-H bonds to nitrogen per nitrogen atom.

The reactivity of all the other units are very similar despite the fact that their sensitiser potentials vary. We must therefore conclude that the reactivity of an amine synergist goes far beyond its primary reaction with the excited triplet state of the initiator.

NMDEA	:	2%Irg-907/10% NMDEA/TMPTA
DMP	:	2%Irg-907/10% Dimorpholinopropane/TMPTA
MM	:	2%Irg-907/10% N-Methylmorpholine/TMPTA
ME	:	2%Irg-907/10% 4-Morpholinoethanol/TMPTA
IPR	:	2%Irg-907/10% Isopropylpyrrolidine/TMPTA
IPP	:	2%Irg-907/10% Isopropylpiperidine/TMPTA

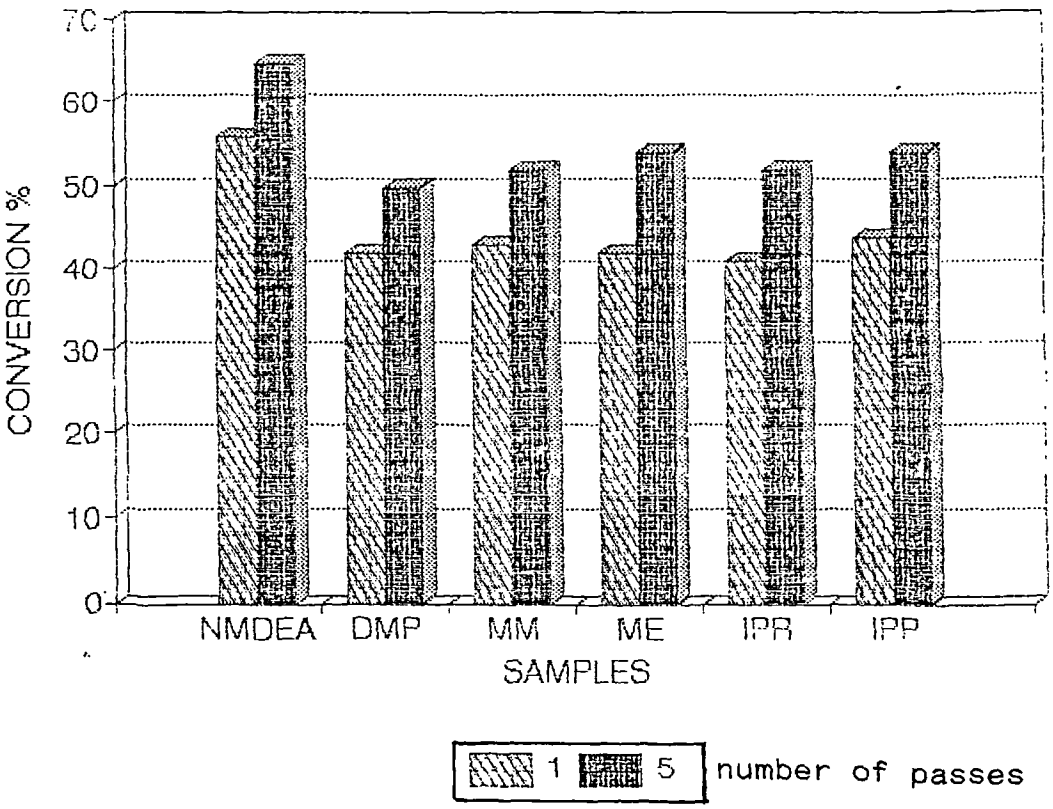


Fig 8.17 The Conversion% of Amines using RTIR Spectroscopy

Photo-DSC Results

Differential Scanning Calorimetry (Photo-DSC) was employed to test the aminoalcohols. Two different acrylate systems, Trimethylolpropanetriacrylate (TMPTA) and Laurylacrylate (LA) were used. Irg-651 (2,2-Dimethoxy-2-phenylacetophenone) and Irg-907(2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propane -2-one were chosen as Type I initiators. The samples were tested under nitrogen, the aim was to see if aminoalcohols had any effect on Type I initiators. Therefore to eliminate the oxygen scavenging ability of amines and aminoalcohols, oxygen was removed and replaced by nitrogen for the photo-DSC experiments.

The area of the peaks ($\triangle H$) was calculated as cal/g. The sample 2% Irg-907/LA (Fig. 18) gave 64.66 cal/g heat out, When the aminoalcohol S-(-)-N-Methyl-1,1-Diphenylprolinol (AA4) was added to this mixture at 1% level, the heat output slightly increased to 70.35 cal/g (Fig.8.19); this may be due to aminoalcohols reducing Irg-907. Presumably, with Irg-907, the aminoalcohols are hardly affecting the reactions. Although the areas of the other two aminoalcohols, 2-Methyl-1-[4-(Methylthio)phenyl]-2-morpholino-propane-1-ol (1ROL) (Fig.8. 20) and 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-ol (MOROL) were not calculated, their exotherms showed similar efficiency (Fig. 21).

The aminoalcohol, S-(-)-N-Methyl-1,1-Diphenylprolinol was tested using RTIR spectroscopy, 58% of conversion was obtained for 84 sec of irradiation. This value is even better than that obtained with 10% NMDEA where the conversion value was 56%.

The DSC results are given in Figs.8.22-25. In the case of Irg-651, the addition of 1% aminoalcohols to the mixture does not seem that these aminoalcohols had any effect on Type I initiator in the absence of oxygen.

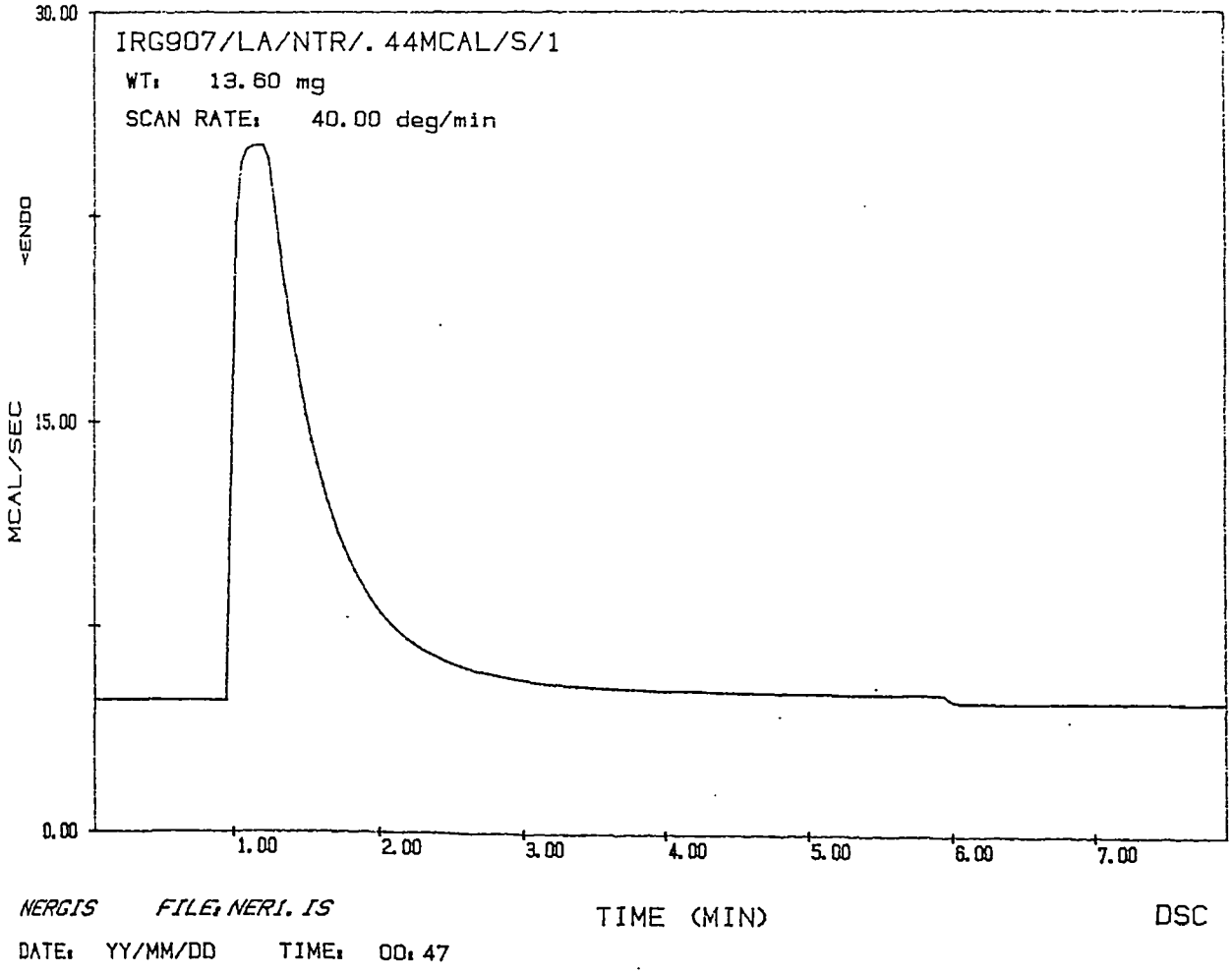


Fig 8.18 DSC trace for photopolymerisation of 2% IRG-907/LA in nitrogen.

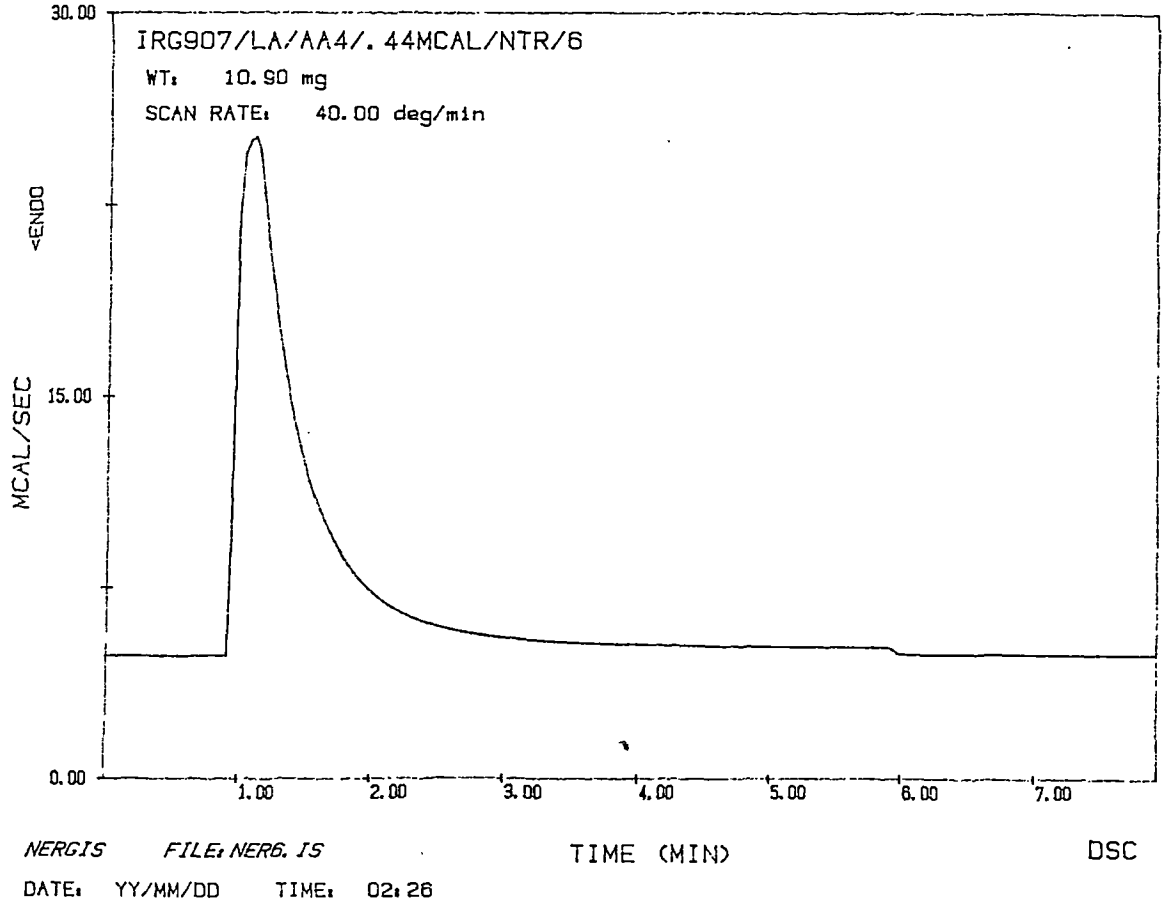


Fig 8.19 DSC trace for photopolymerisation of 2%IRG-907/ 1% S-(-)-N-Methyl-1,1-Diphenylprolinol (AA4)/LA in nitrogen.

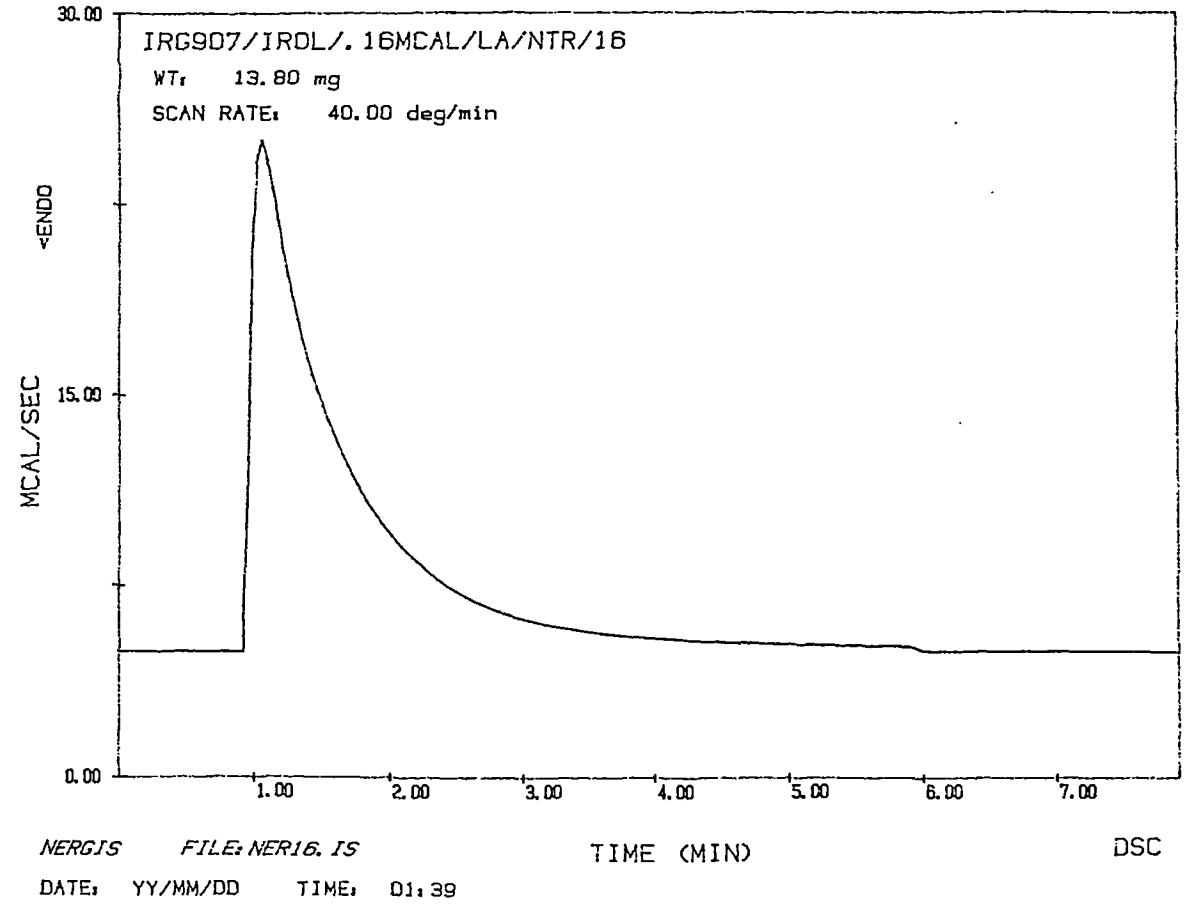


Fig 8.20 DSC trace for photopolymerisation of 2-Methyl-1-(4-(Methylthio)phenyl)-2-morpholino propane-1-ol(IROL) presence of 2% IRG-907 in nitrogen.

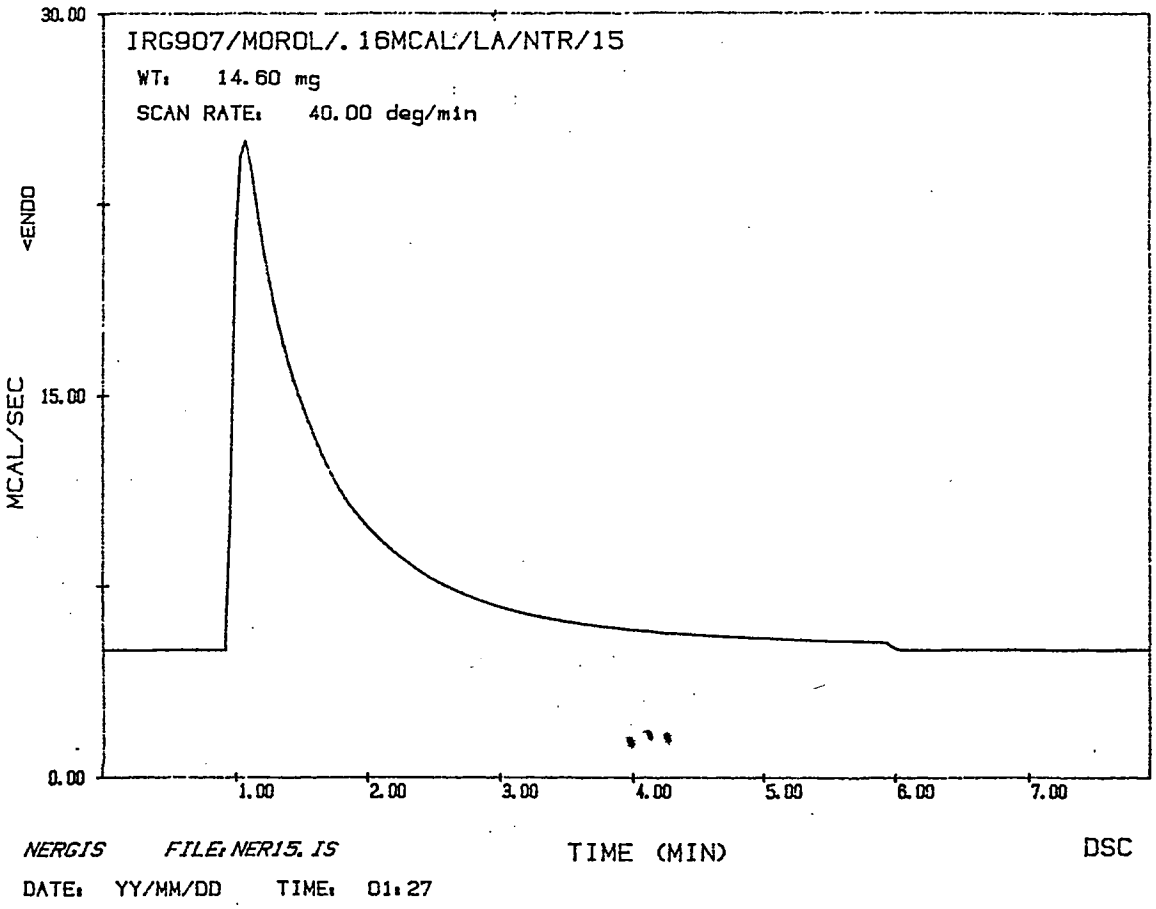


Fig 8.21 DSC trace for photopolymerisation of 2%IRG-907/ 1% 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-ol (MOROL)/LA in nitrogen.

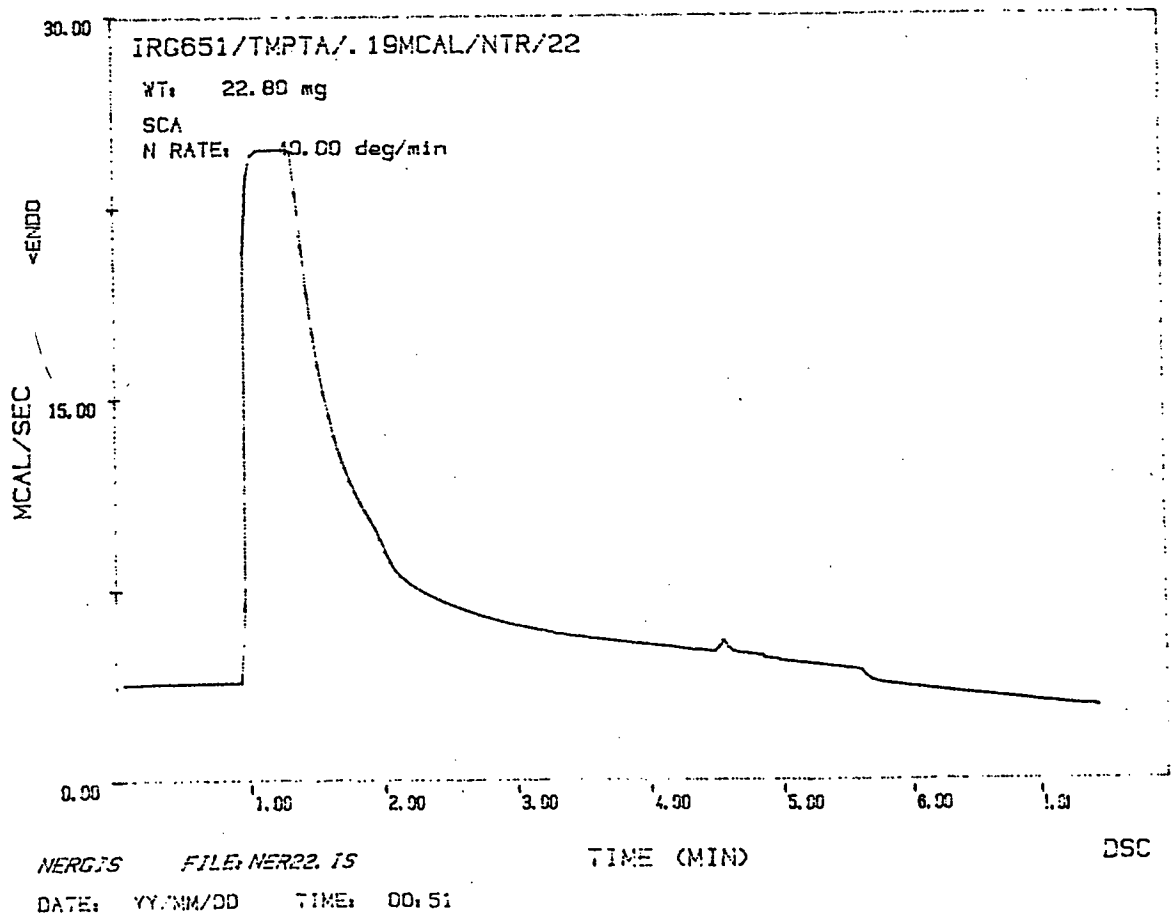


Fig 8.22. DSC trace for photopolymerisation of 2% IRG-651/LA in nitrogen.

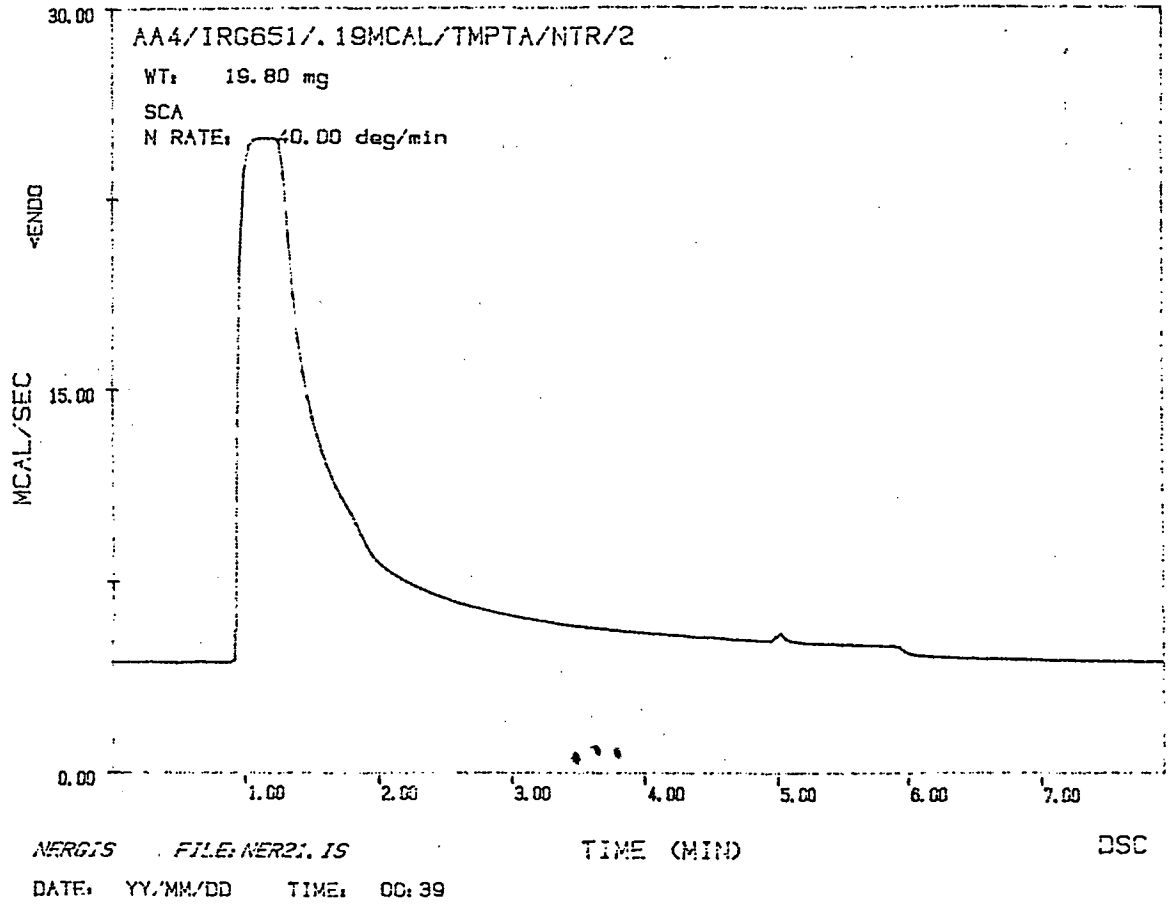


Fig 8.23. DSC trace for photopolymerisation of 2% IRG-651/S-(-)-N-Methyl-1,1-Diphenylprolinol (1%) (AA4)/LA in nitrogen.

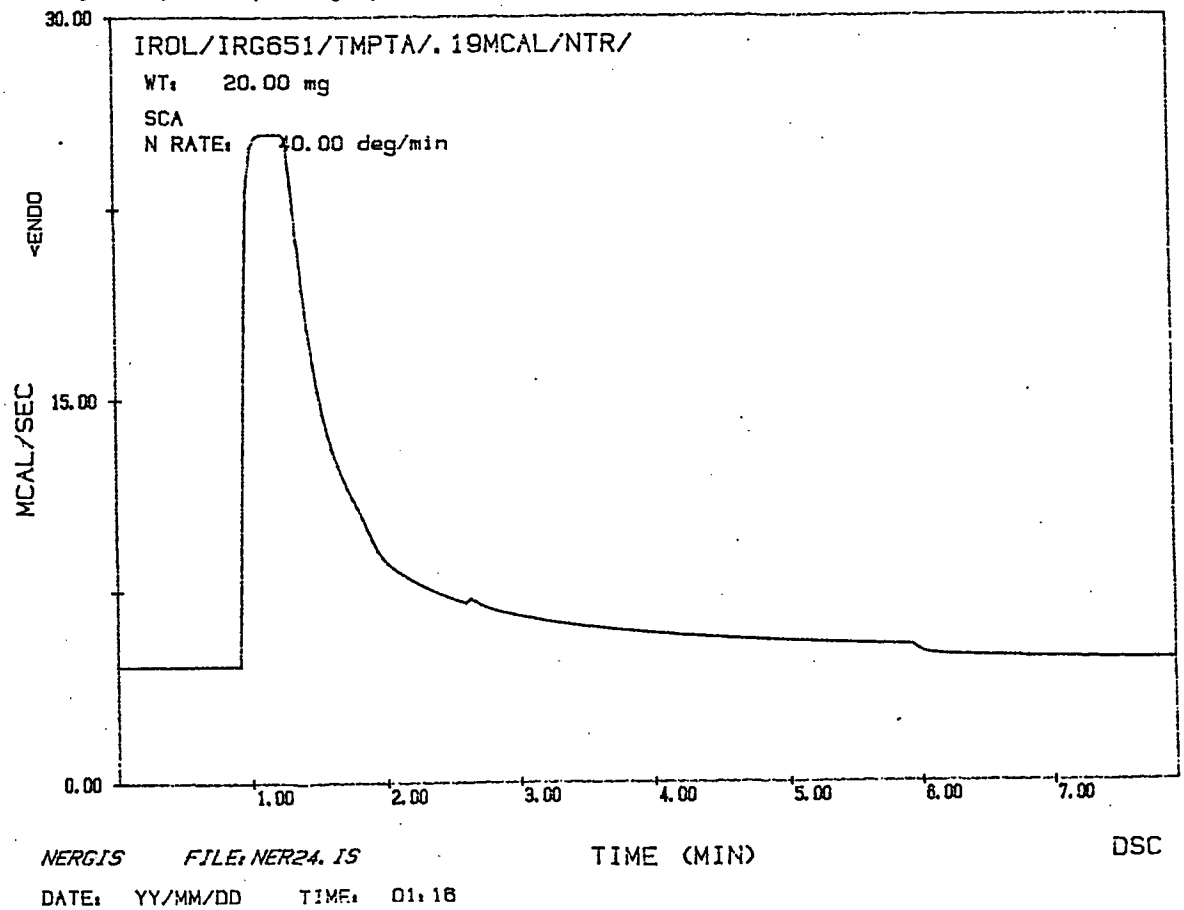


Fig 8.24. DSCtrace for photopolymerisation of 2% IRG-651/ 1% 2-Methyl1-(4-(Methylthio)phenyl)-2-morpholinopropane-1-ol (IROL) in nitrogen.

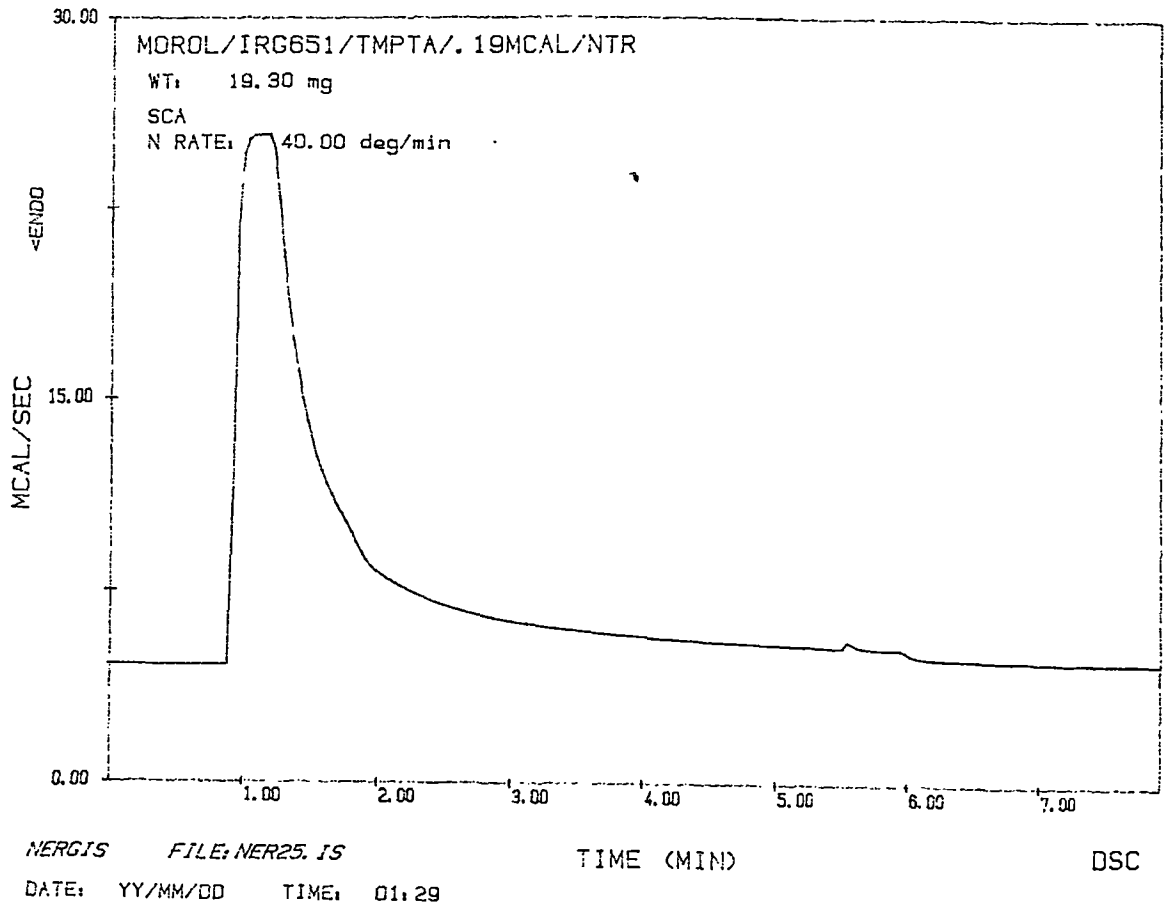


Fig 8.25. DSC trace for photopolymerisation of 2% IRG-651/1% 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-ol (MOROL) in nitrogen.

EXPERIMENTAL

Materials

N-Methyldiethanolamine, TMPTA, and Benzophenone were obtained from Aldrich Chemical Company Irg-907 and Irg-651 were supplied by Ciba Geigy S-344 (Polyethylene glycol (400) diacrylate) and S-259 (Polyethylene glycol (200) diacrylate were obtained from Cray Valley and P.4094 (Aliphatic - trifunctional acrylate) and P.4149 (Aliphatic trifunctional acrylate) were obtained from Harcross Chemical Company .

The information about techniques, RTIR, Bulk Polymerisation, FTIR, DSC and Pendulum Hardness, was given in Chapters 4, 3, 6, 5 and 5 respectively.

Personal Acknowledgement

I would like to thank most sincerely from the bottom of my heart my good friend Dr Patricia Moran for all her advice, guidance, patience, kindness, care and support throughout the duration of my PhD studies.

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CHAPTER 9

EFFECT OF AMINOALCOHOLS PHOTOSTABILITY OF COATINGS

Chapter 9. EFFECT OF AMINOALCOHOLS PHOTOSTABILITY OF COATINGS

EFFECT OF AMINOALCOHOLS, PHOTOSTABILITY OF COATINGS

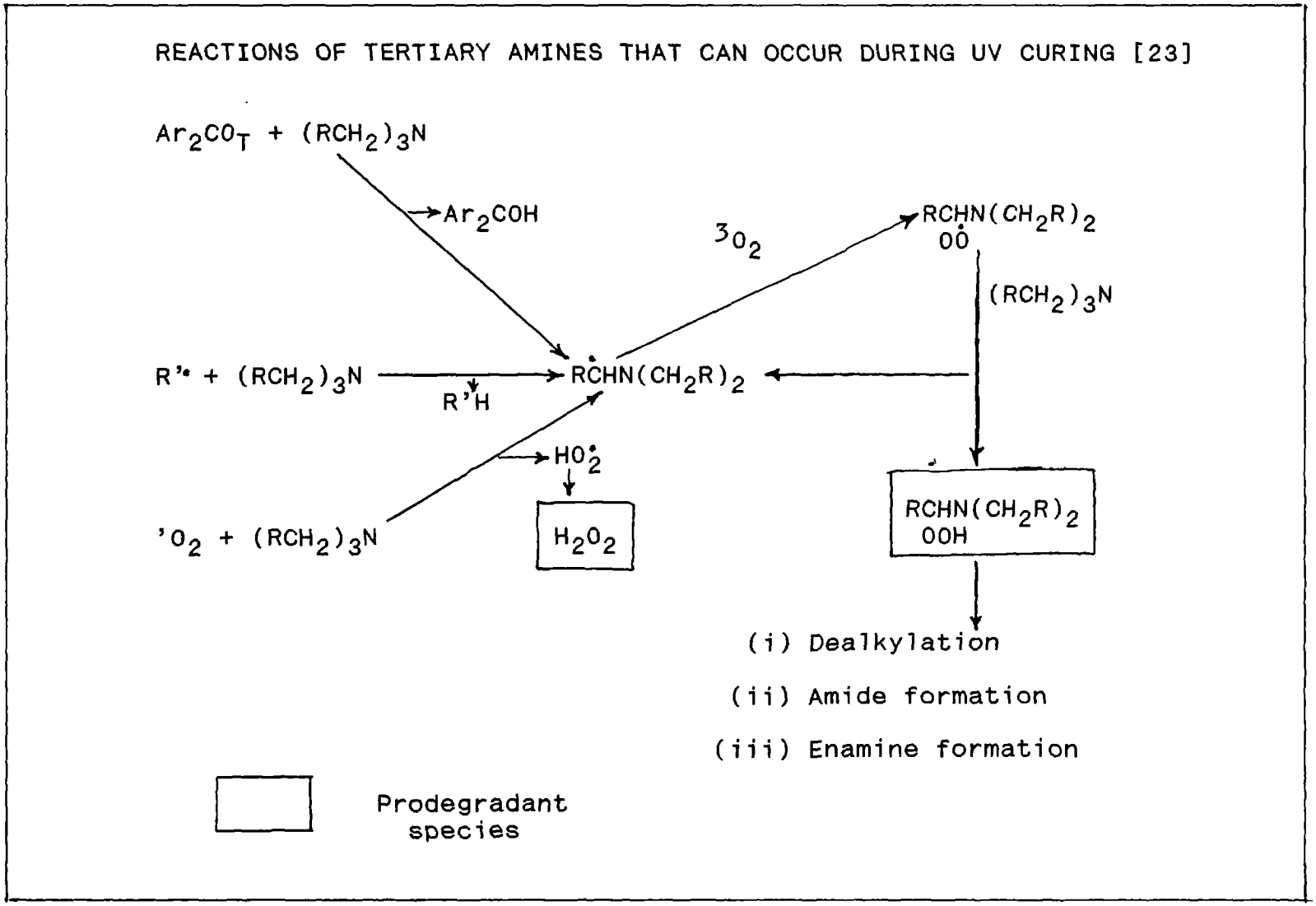
INTRODUCTION

A number of studies have been carried out to investigate the photo-oxidation and photoyellowing phenomena which occur in various multifunctional acrylated systems [1-16]. The complex formulations of radiation curable resins complicate our understanding of the mechanisms involved. For example, high concentrations of photoinitiators in UV curable resins will often dominate the subsequent photoreactions and contribute significantly to photoyellowing. With regard to photo-oxidative stability, hydrogen abstracting type photoinitiators such as benzophenone are more detrimental than the photofragmenting types such as the benzoin ethers [2-7]. Other factors include the use of tertiary amines as co-synergists, which also contribute towards the photoyellowing phenomenon and photostability of the resin and these may be free or reacted with acrylate groups in the resin.

In earlier studies [14,15], it was found that whilst the use of tertiary amines contributed significantly toward the subsequent photoyellowing of resins, they nevertheless markedly improved their photo-oxidative stability.

The effectiveness of amines as a synergist and as a reducer of oxygen inhibition lies in the reactivity of the C-H bonds

SCHEME 1


REACTIONS OF TERTIARY AMINES THAT CAN OCCUR DURING UV CURING [23]
$Ar_2CO_T + (RCH_2)_3N$
Ar_2COH
$^3O_2$
$RCHN(CH_2R)_2$
OO
$(RCH_2)_3N$
$R'^{\bullet} + (RCH_2)_3N$
$R'H$
$RCHN(CH_2R)_2$
$HO_2^{\bullet}$
$^1O_2 + (RCH_2)_3N$
H_2O_2
$RCHN(CH_2R)_2$
OOH
(i) Dealkylation
(ii) Amide formation
(iii) Enamine formation
Prodegradant species

α to the nitrogen atom [17]. The reactions of the tertiary amines are summarised in Scheme I. Factors which influence the efficiency of these reactions include the ionisation potential of the amine, the stability of the α-aminoalkyl radical and the acidity of the α-C-H bond.

It will be seen from Scheme I that the use of tertiary amines leads to the production of prodegradant species. The α-hydroperoxyamines are very reactive and decompose to give a range of highly coloured, uncharacterised products. N-Methyldiethanolamine, which is an excellent synergist has been shown to promote photoyellowing [18]. The use of ITX with this amine to polymerise an acrylated urethane and an acrylated epoxy gave films which yellowed rapidly upon irradiation and the ITX was held as being primarily responsible for this process.

There is now good evidence to support the view that the yellowing of cured films containing amines is partly due to the amine component [15,16,19,20,21,22]. The yellow products so formed can in many cases be photobleached. There is much evidence to support the theory that the yellowing is due to the amine, and the oxidative degradation of the resin may not be directly related. The presence of tertiary amines in the cured film helps to photoreduce any residual Type II photoinitiators and so protect the coating.

It is also claimed that the formation of hydroperoxides does not enhance the oxidative degradation of the coating since reduction of the hydroperoxides by sulphur dioxide does not photostablise the coating [15]. Amine terminated acrylates also lead to a reversible yellowing reaction. It has been demonstrated that the structure of the amine is related to the extent of yellowing [22]. Thus for a series of amines to cause yellowing, the following order of reactivity was found:-

dibutyl=diethylamine=dimethylamine>morpholine>
dicyclohexylamine>N-ethyl ethanolamine>N-methyl
ethanolamine.

The inclusion of tertiary amines in UV and EB curing formulations produces films which will discolour on weathering but these amines may well intercept radical processes which are deleterious to the performance of the coating.

In addition, the formation of yellow-coloured species near the surface of the film may offer some protection due to the species by acting as a UV screen.

WEATHERING OF UNPIGMENTED RADIATION CURED FILMS

Polymers which are used on a large scale have been divided into three groups which reflect their resistance to photo-degradation [24]:

(a) Highly photostable materials that are commonly used without added stabilisers e.g. polytetrafluoroethylene and poly(methyl methacrylates).

(b) Moderately photostable polymers that can be used without stabilisers e.g. poly(ethylene terephthalate) and polycarbonates.

(c) Poorly photostable polymers which need extensive stabilisation for outdoor uses e.g. polyolefins, poly(vinyl chloride), polystyrene, polyamides, polyurethanes, polybutadienes etc.

The term 'photostable' is somewhat enigmatic and very few of the materials listed above are truly photostable to extensive outdoor weathering. Breakdown of films manifests itself in a number of ways such as, loss of surface gloss, crazing the surface, increase in brittleness, pitting of the surface and weight loss. Many of the polymers might be expected to show much better resistance to weathering on the grounds that they should absorb little if any solar radiation (Fig 9.1). Solar radiation contains very little in the wavelength range 300-350nm and most of the polymers should not absorb within this range. However, due to the presence of catalyst residues and build up of peroxidic species and their breakdown products during preparation, the polymers do exhibit a finite

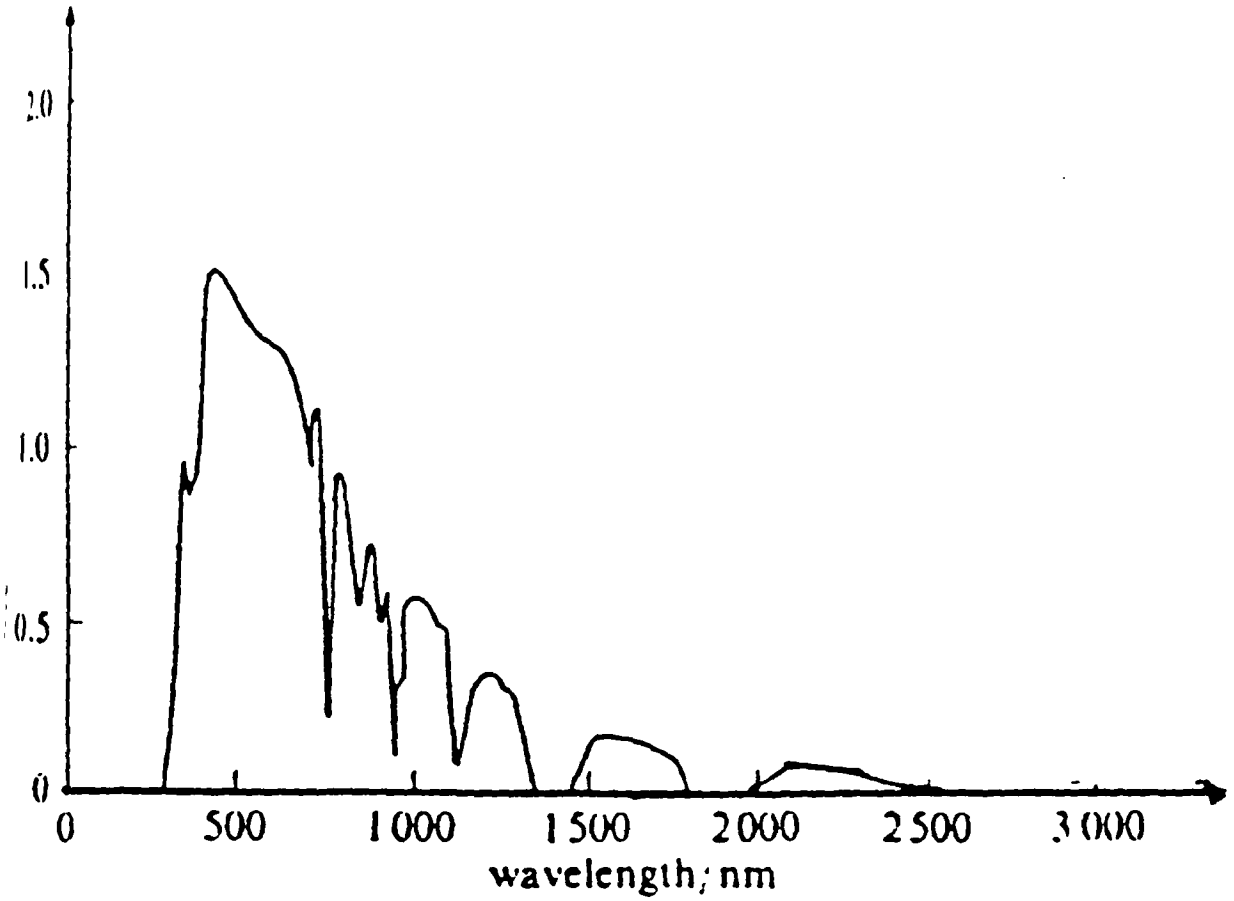


Fig 9.1

absorption within this wavelength range.

Radiation curable formulations contain oligomers and reactive diluents. In the case of free radical curable systems, the formulations are usually based on acrylates and to a lesser extent, methacrylates. A hazard commonly encountered with the preparation of such materials is that they will undergo thermal polymerisation, and consequently, during preparation the reaction mixtures are continuously sparged with oxygen which may lead to incorporation of peroxidic species.

For the most part, radiation curing is carried out on films laid down in the atmosphere as opposed to under nitrogen or under vacuum, and as a consequence, the films, prior to curing contain oxygen. Thus, when curing is carried out, some peroxidic species will be produced due to the growth of the polymer chains being terminated by dissolved oxygen in the film.

$$M^* \longrightarrow (M)_nM^* \xrightarrow{O_2} (M)_nMOO^*$$

M^* = Monomer radical

Not surprisingly therefore, it is found that surface coatings produced by radiation curing do not possess particularly good weathering properties.

In the scenario just described, the origin of the photochemical instability is chemical i.e. build up of centres of instability due to chemical reaction. Another potential source of instability is the structure of the oligomer backbone e.g. in the case of polycarbonates [25] and polyurethanes [26]. When considering UV curing of systems polymerised via free radicals, there is a host of other chemical sources which can lead to poor weathering characteristics e.g. residual photoinitiator, photoinitiator decomposition products, synergist and synergist degradation products and residual unpolymerised functional groups (e.g. acrylates). These processes are summarised in Scheme 1.

Physical factors also play an important part in determining how efficiently the chemical processes may take place. Some of these factors are within the control of the formulator e.g. the crosslink density [27]. Other factors are not only less easy to control but are also less understood e.g. the homogeneity of the coating. It is now known that curing of diluent/oligomer mixes occurs in distinct phases and that islands of highly crosslinked materials separated by more fluid areas and containing unreacted reactive groups may be produced [28]. It is also possible that the coating will contain crystalline and non crystalline regions. The physical structure of the film can also be affected by whether the curing is carried out at a temperature above or below the

Tg of the surface coating. Not surprisingly other factors such as oxygen permeability, the thickness of the film, the reflectivity of the substrate and the strength of the adhesive bond between the coating and the substrate play an important role.

Initiation of degradation is often due to impurities introduced by the curing process, particularly carbonyl compounds and peroxides, photosensitisers acting as prodegradants. Clearly if the oligomer backbone contains photosensitive groups then the films have a built in prodegradant group.

Factors influencing the physical properties of the film

A major process is the formation of hydroperoxides and this increases the hydrophilicity of the surface and the brittleness of the film. Fragmentation of the tertiary alkoxy radicals leads to chain scission and hence a decrease in molecular weight which manifests itself as a decrease in tensile strength but an increase in elongation. Inter-chain radical radical combination produces crosslinks which increases brittleness and decreases elongation. Crosslinking processes can lead to cracking of films.

To summarise, the photodegradation may occur via photo-

oxidative degradation and photocrosslinking at the surface. The crosslinking may lead to cracks in the film thereby enhancing oxygen access to the polymer with the consequence that photo-oxidative degradation takes place both within the film and at the film substrate interface. Crosslinking will also adversely affect the adhesive bond between the coating and the substrate.

RESULTS AND DISCUSSION

The ability of amines and aminoalcohols to act as a synergist in a Type II reaction, to act as an ameliorator of oxygen inhibition and to promote yellowing in cured films are all linked.

In this chapter, the photoyellowing and photo-oxidation of aminoalcohols are investigated. For this study, different aminoalcohols were synthesised for which the preparation methods are given in detail in Chapter 2 . The list of aminoalcohols, including their structures are given in Table 9.1 (page 251a).

The effect of initiators on yellowing and the synergistic effects of aminoalcohols were also investigated and the results are described in Chapters 5 and 8 , respectively.

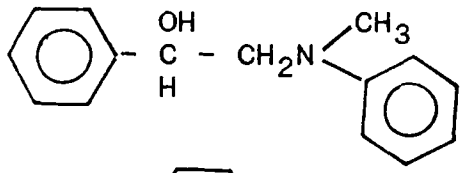
Initially, the effectiveness of the various aminoalcohols on photoyellowing was compared in benzophenone-epoxyacrylate/TPGDA formulation, for different Q-UV exposure times. All formulations which contain aminoalcohols were also compared with N-methyldiethanolamine. Maximum Q-UV exposure time was defined as 500 hours.

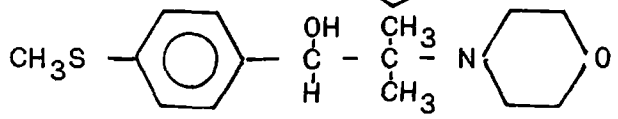
In this study all weathering experiments were carried out

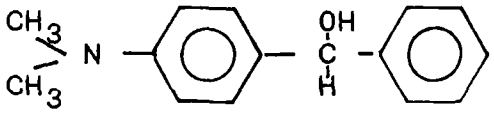
Table I

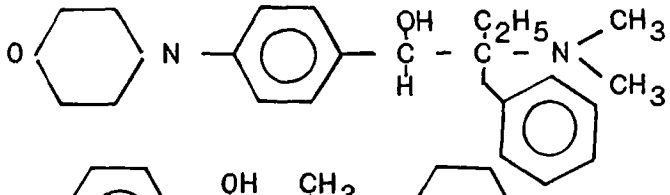
The list of aminoalcohols which are used in the following formulations:-

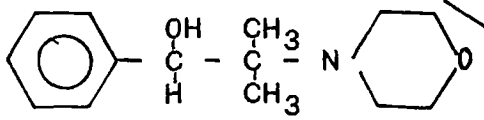
E1 : $CH_3N(C_2H_5O)_2$

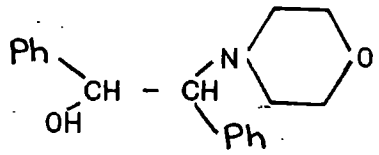
E2 :  ≠BP ≠ EA ≠ TPGDA

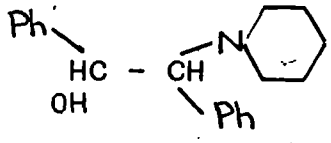
E3 :  ≠BP ≠ EA ≠ TPGDA

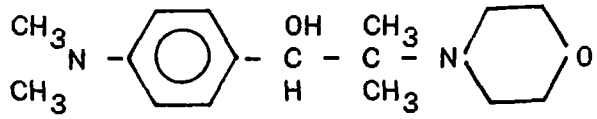
E4 :  ≠BP ≠ EA ≠ TPGDA

E5 :  ≠BP ≠ EA ≠ TPGDA

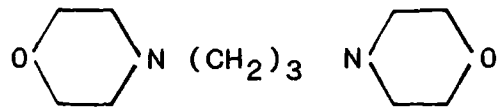
E6 :  ≠BP ≠ EA ≠ TPGDA

E7 :  ≠BP ≠ EA ≠ TPGDA

E8 :  ≠BP ≠ EA ≠ TPGDA

E9 :  ≠BP ≠ EA ≠ TPGDA

E10 : BP + EP + TPGDA

E11 :  ≠BP ≠ EA ≠ TPGDA

Where:

BP : Benzophenone

EA : Epoxyacrylate

TPGDA : Tripropyleneglyroldiacrylate

using a Q-UV weatherometer with a UV-A340 fluorescent lamp attached to the Q-UV. The spectrum of UV-A340 is given in Fig 9.2. The UV-A340 is the best available simulation of sunlight in the critical, short wavelength region.

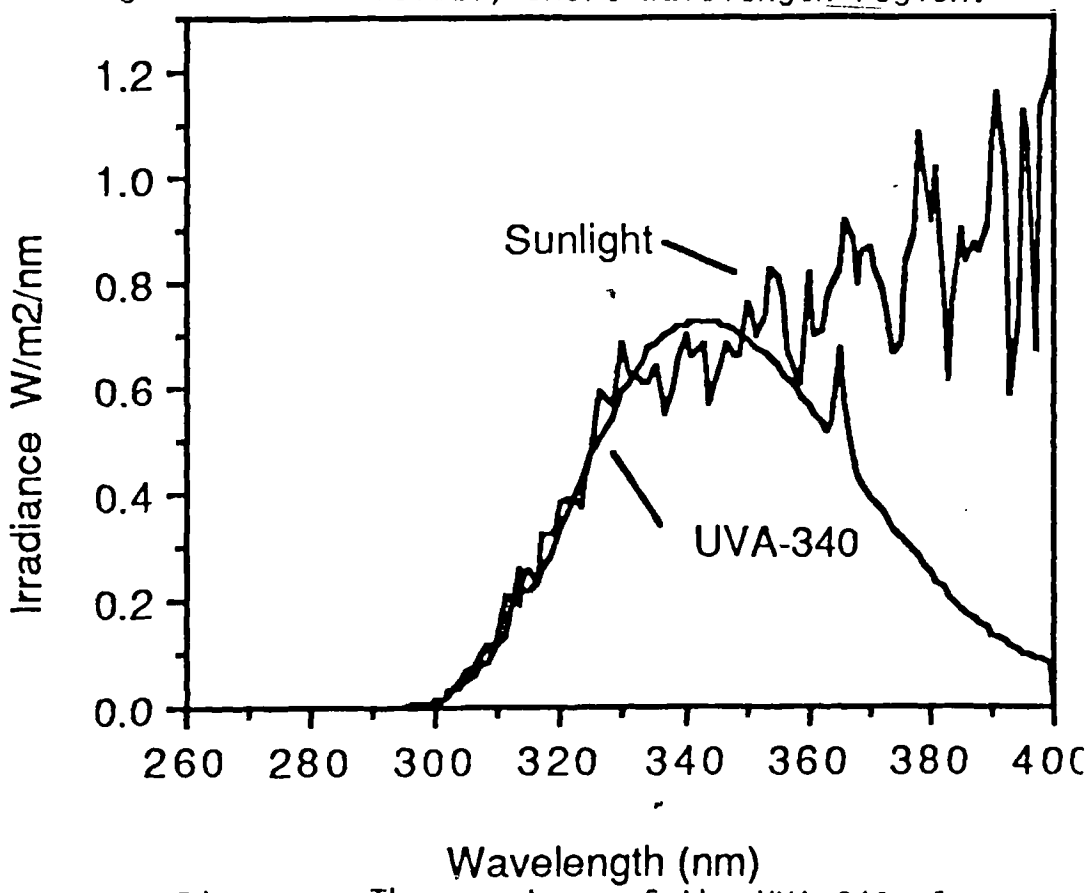


Fig 9.2 The spectrum of the UVA-340 lamp

All samples were subjected to a continuous cycle of UV (4 hours) and condensation for 4 hours

The yellowing indices were determined for each sample before and during Q-UV exposure times and the results are shown in Figs.9.3 and 4.

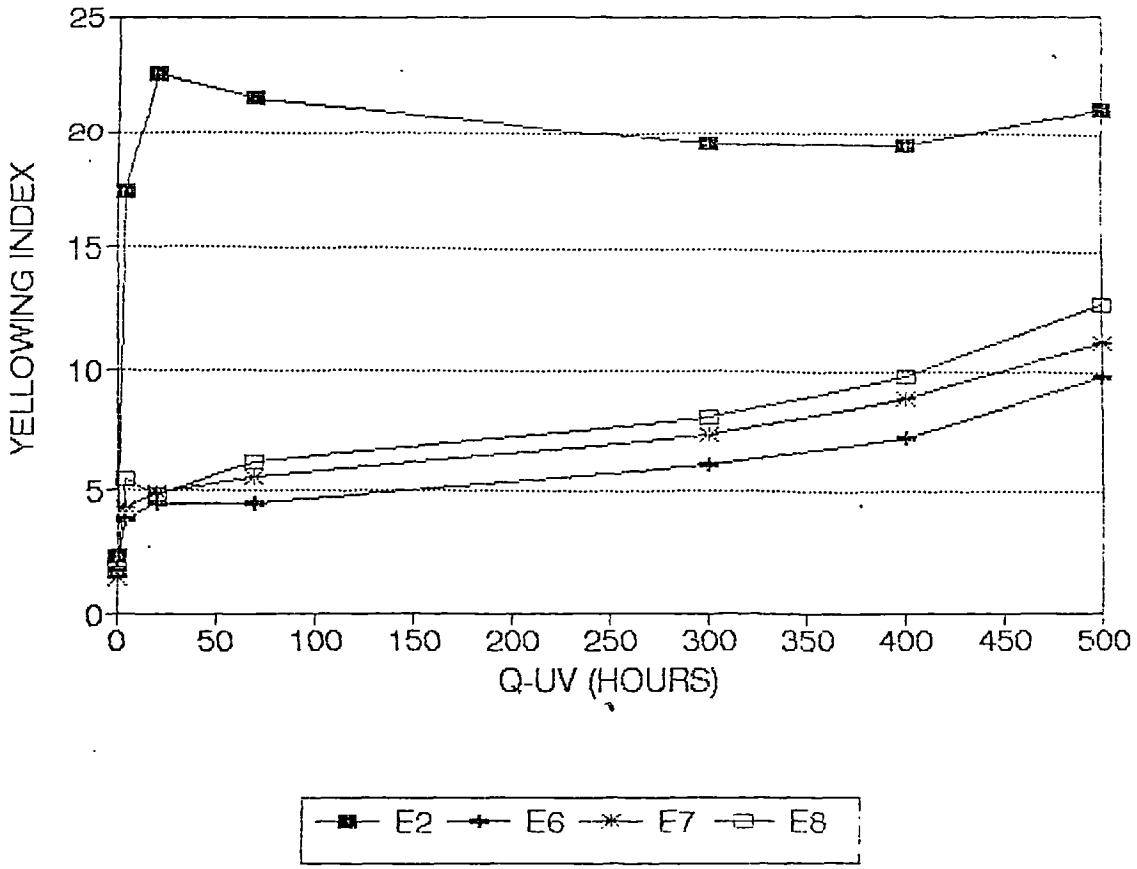


Fig 9.3 The yellowing indices for samples E2, E6, E7 and E8 during Q-UV exposure hours

As can be seen from Fig 9.3, the yellowing index of E2 reached over 20 in 4 hours Q-UV exposure time whereas E6, E7 and E8 had quite low yellowing indices compared to E2. E2 has methyl and phenyl groups adjacent to the nitrogen. As previously mentioned the primary process of photoyellowing is oxidation of the methylene groups adjacent to the nitrogen. In the case of E2 a photobleaching effect was observed during 400 hours of exposure time and then the yellowing started to group again.

For E6, E7 and E8, the yellowing indices increased rapidly to ~5 over 20 hours and then slowly increased on further irradiation.

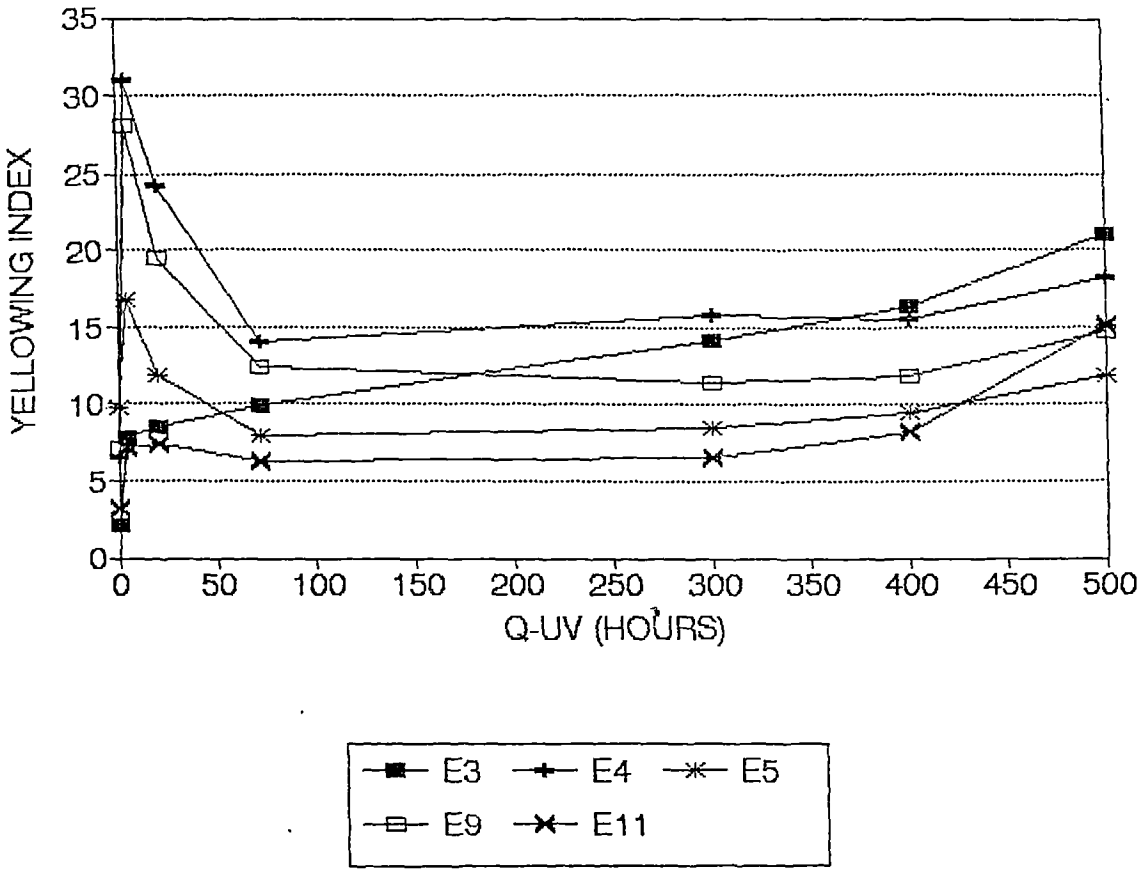


Fig 9.4 The yellowing indices for samples E3, E4, E5, E9 and E11 during Q-UV exposure hours

In Fig 9.4 it will be seen that all the samples show rapid initial yellowing. This is most marked for E4 which has a yellowing index of 32 after 4 hours and then bleaching occurs. Yellowing commences again after approximately 70 hours. A similar behaviour is exhibited by E9 and to a lesser extent by E5. E3 and E11 exhibit much less initial yellowing and continue to yellow on further irradiation at a much reduced rate.

The yellowing indices were also determined for samples containing only benzophenone and benzophenone-N-methyl-diethanolamine as shown in Fig 9.5

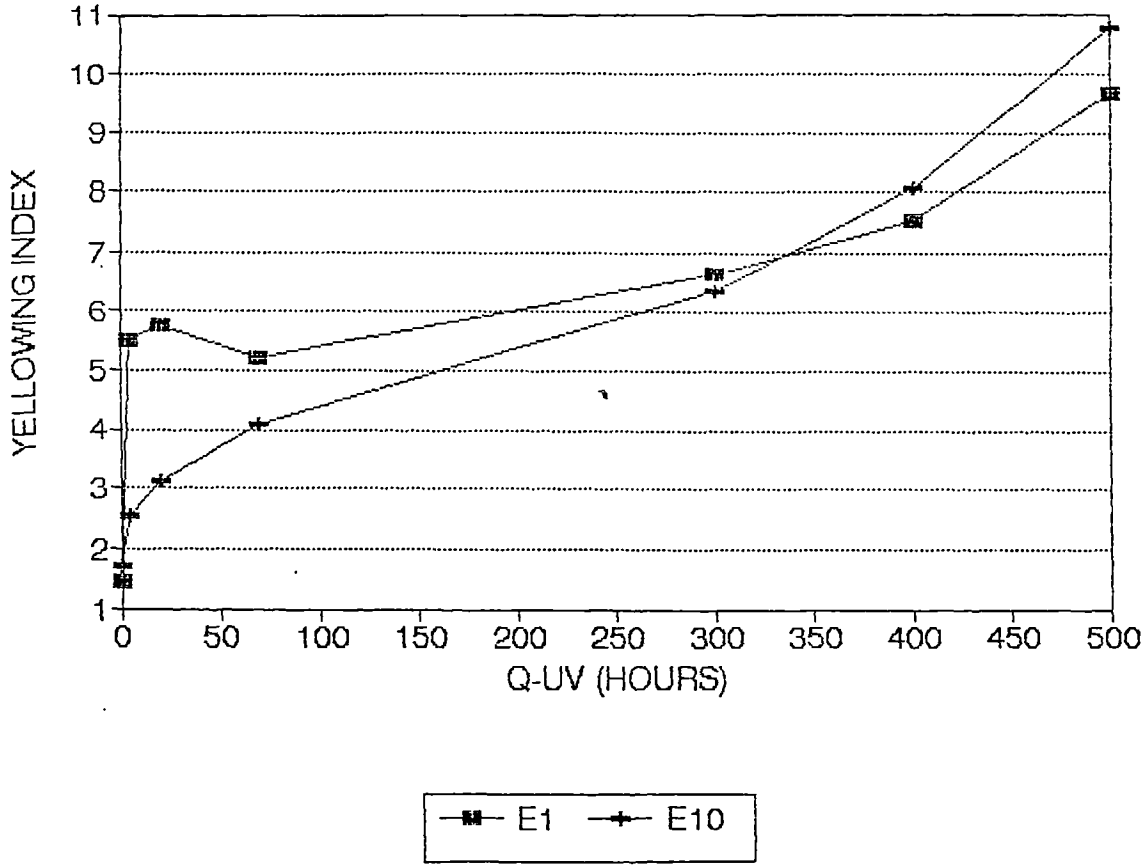


Fig 9.5 The yellowing indices for samples E1 and E10 during Q-UV exposure hours

The formulation E1 which has N-methyldiethanolamine as well as benzophenone showed initial strong yellowing during 4 hours Q-UV exposure time when compared with the formulation E10 which only consists of benzophenone and acrylate mixture.

A slight photobleaching effect was observed for E1 between 20 and 70 hrs of UV exposure where the yellowing effect was

increasing for sample E10. During the 300 hours of UV exposure in Q-UV, the yellowing indices of both samples were nearly the same. When the UV exposure time was prolonged, the yellowing indices of E10 started to increase. This is the result of the degree of yellowing associated with the type of amine used in the formulations. The tertiary amine, N-methyldiethanolamine is not bound into the system and can be lost during ageing by volatilisation. This may account for the reason why cured coatings containing tertiary amine NMDEA are more resistant to photoyellowing [29].

The changes in yellowing were also followed by UV/Vis absorption spectroscopy. The results of this study are given in Fig 9.6 to Fig 9.17. Initial yellowing was observed in Fig.9.10 this is probably due to residual photoinitiator. On initial weathering the residual photoinitiator was removed photochemically within the first 4 hours of irradiation, as can be seen by the loss of photoinitiator absorptions in the UV/Vis spectra.

The most durable systems experience dramatic yellowing. This raises the question as to whether the coloured products produced on weathering by UV are, in fact providing a protective filter within the coating thereby reducing the opportunities of polymer backbone degradation.

E1

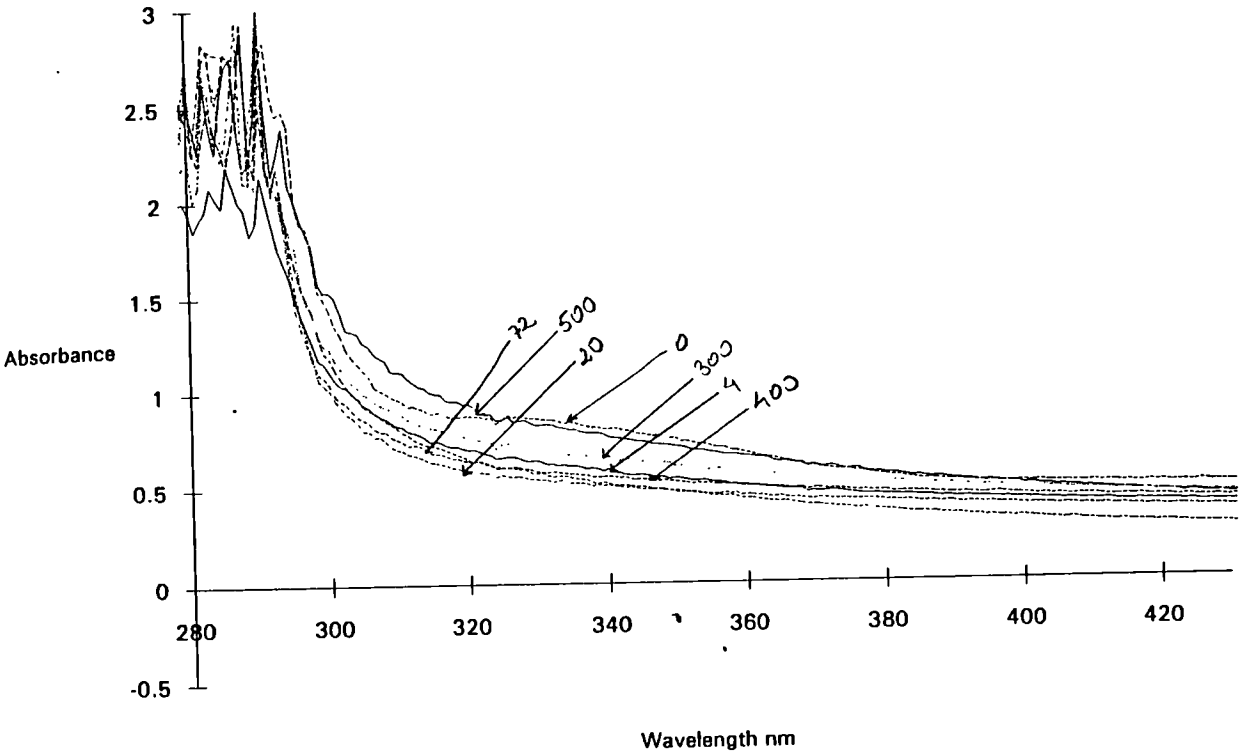


Fig 9.6

E2

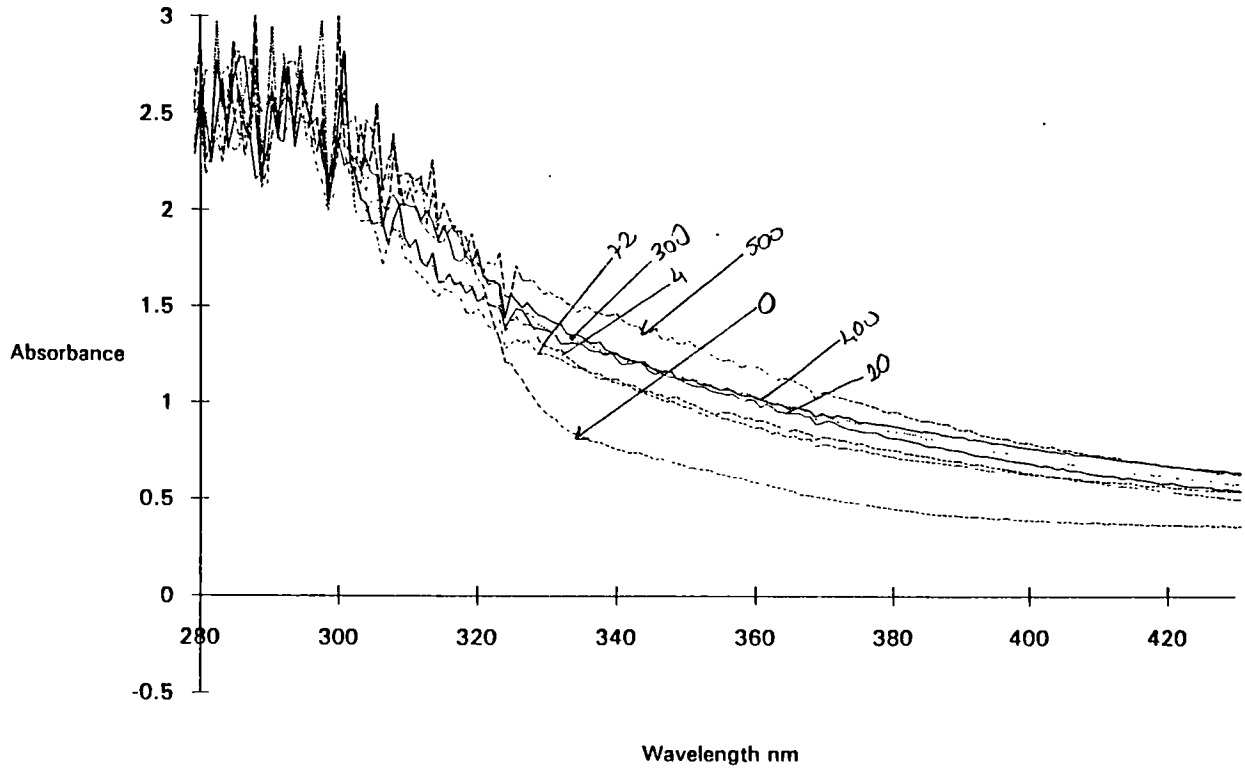


Fig 9.7

E3

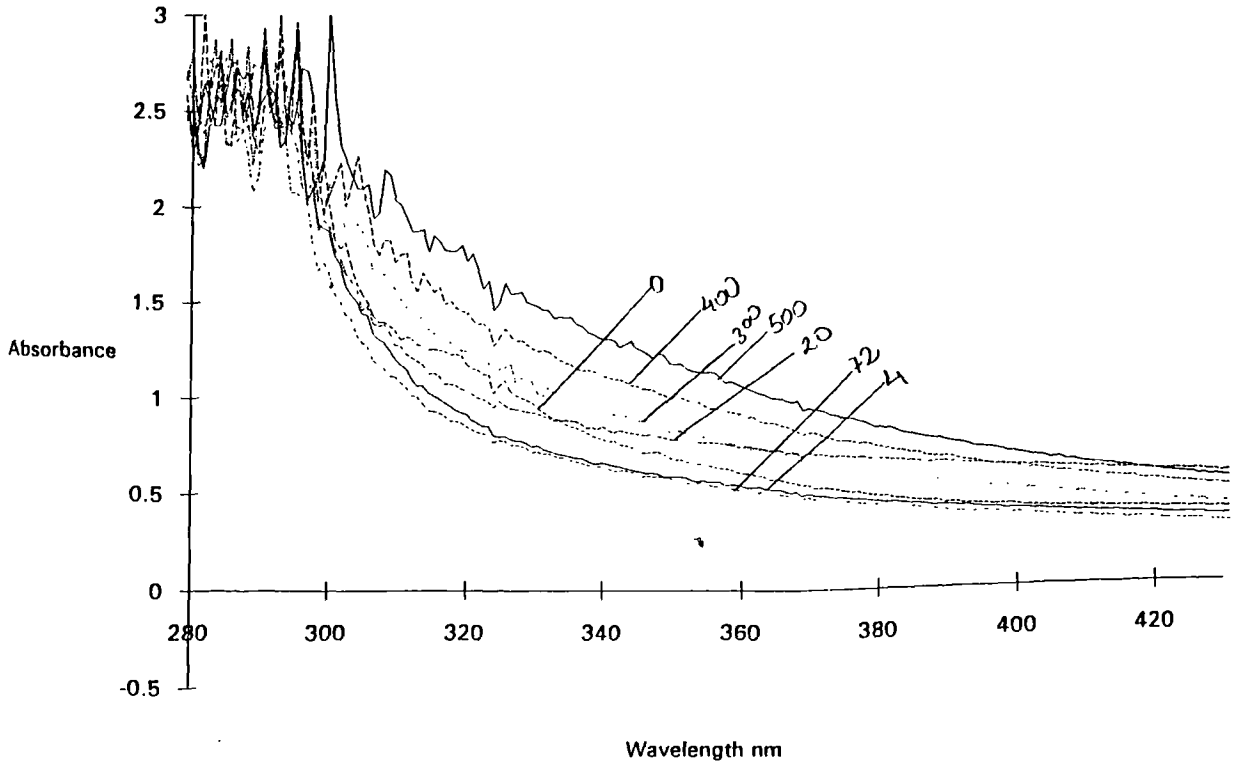


Fig 9.8

E4

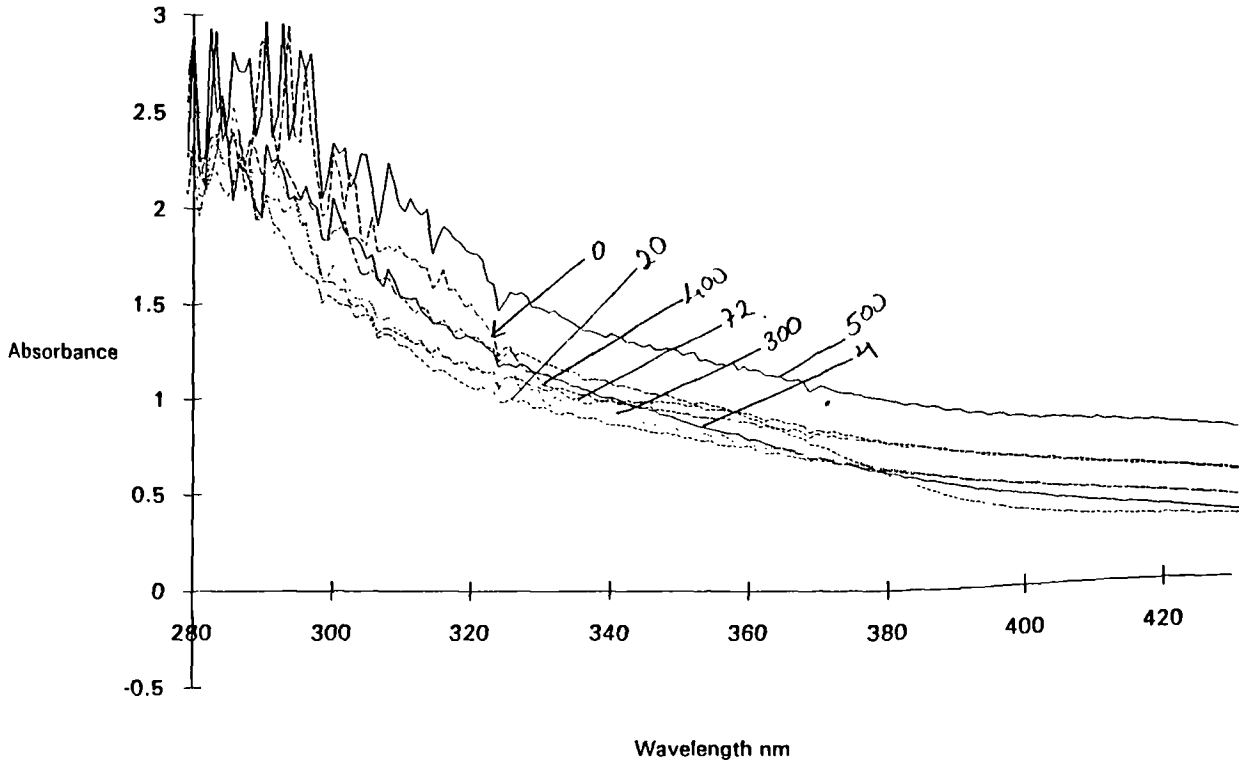


Fig 9.9

E5

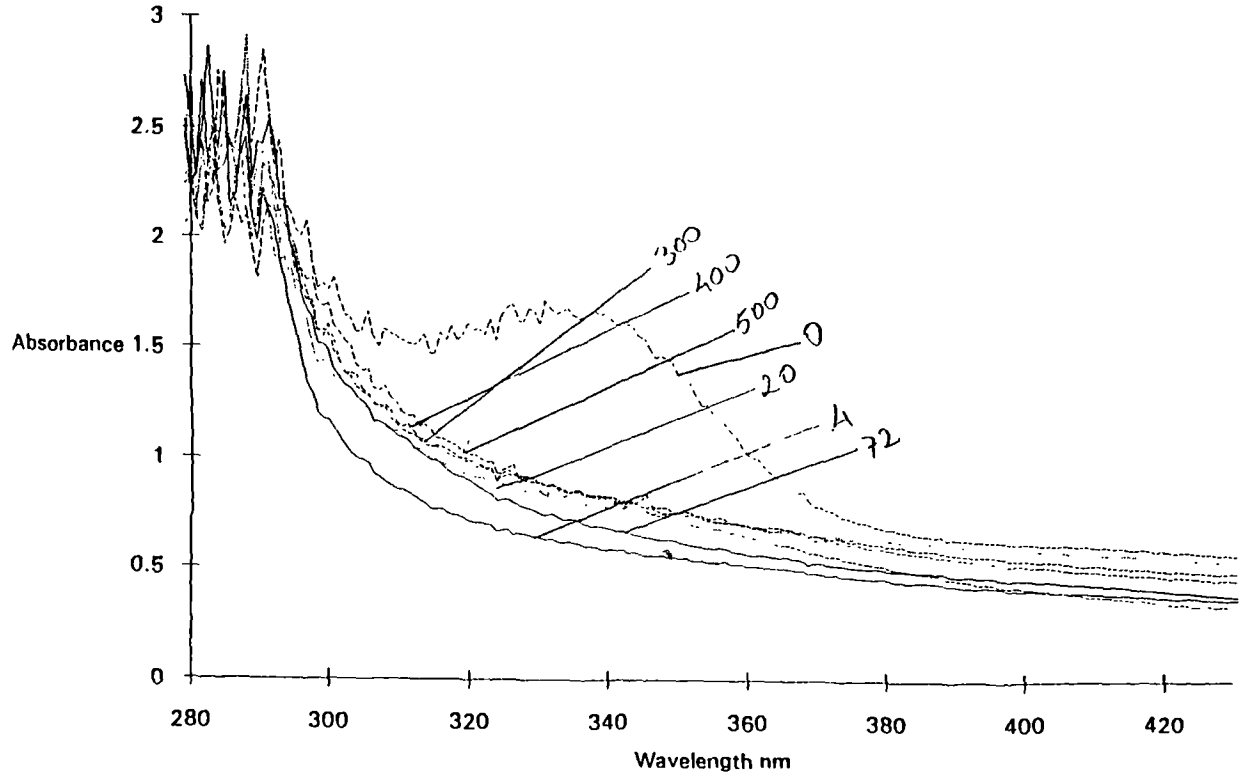


Fig 9.10

E6

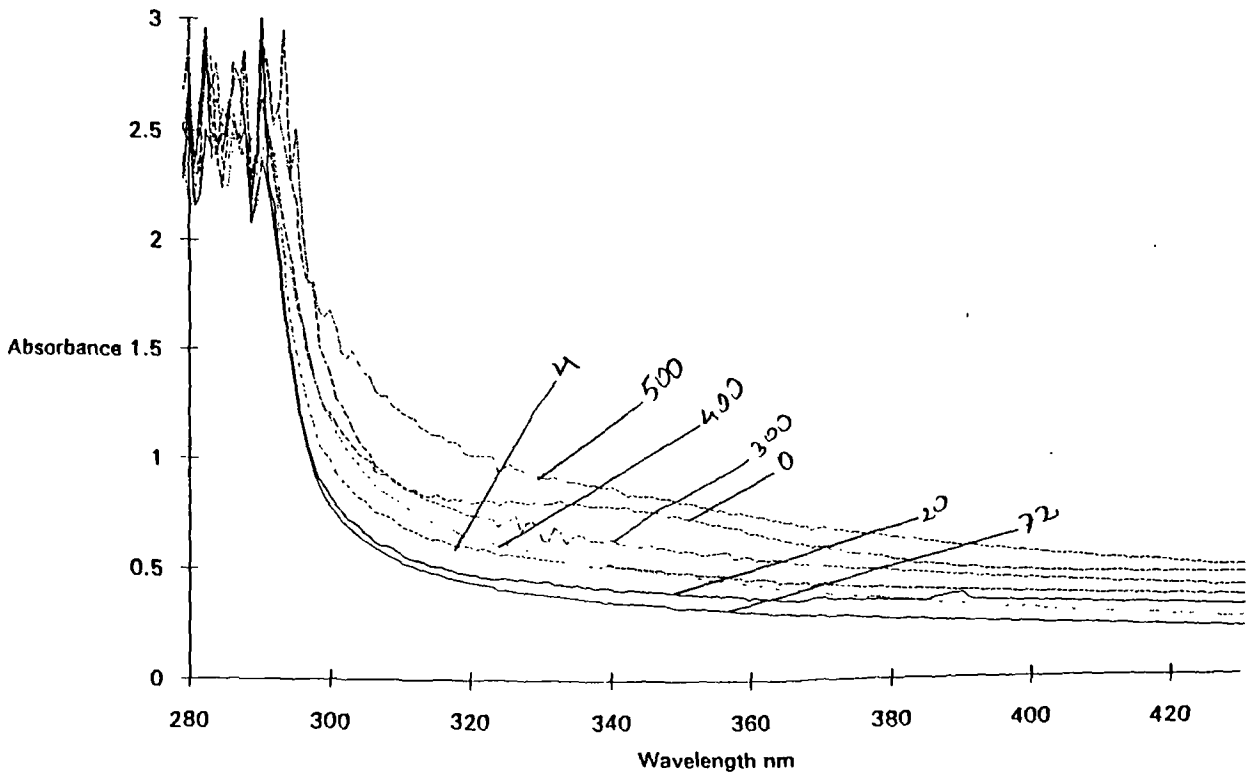


Fig 9.11

E7

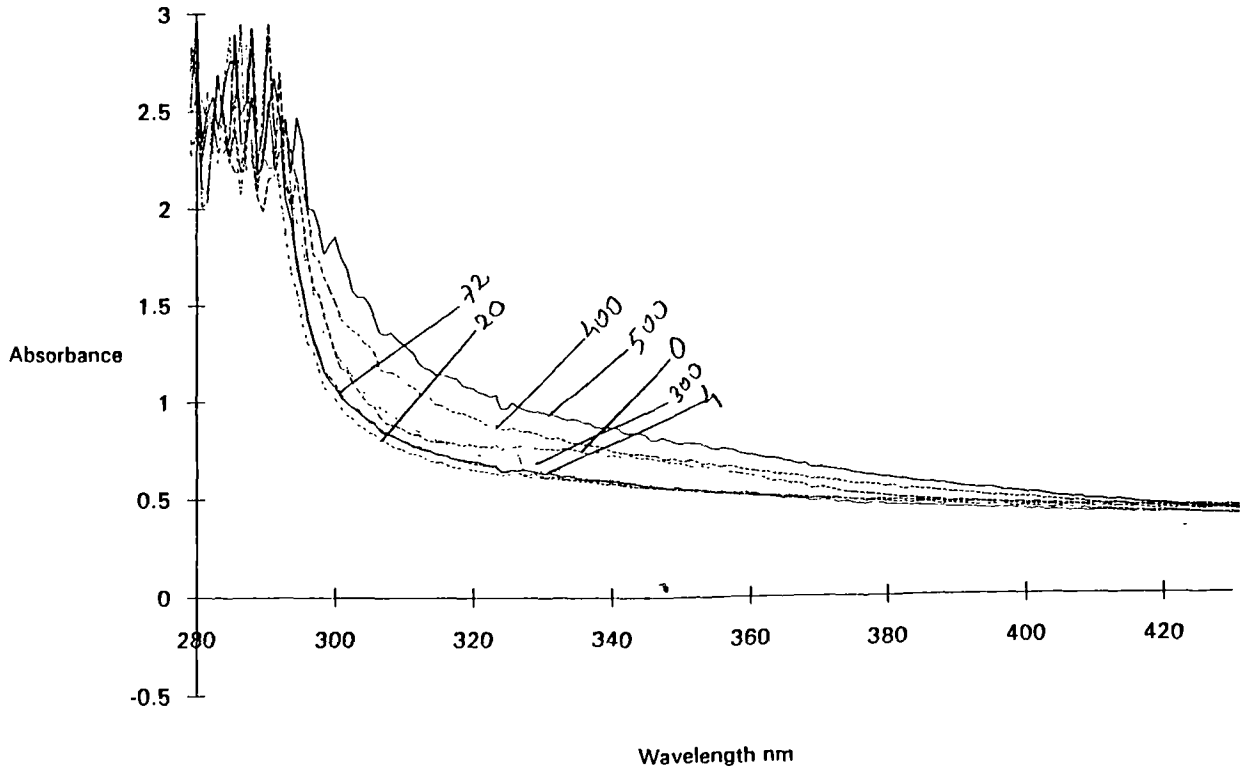


Fig 9.12

E8

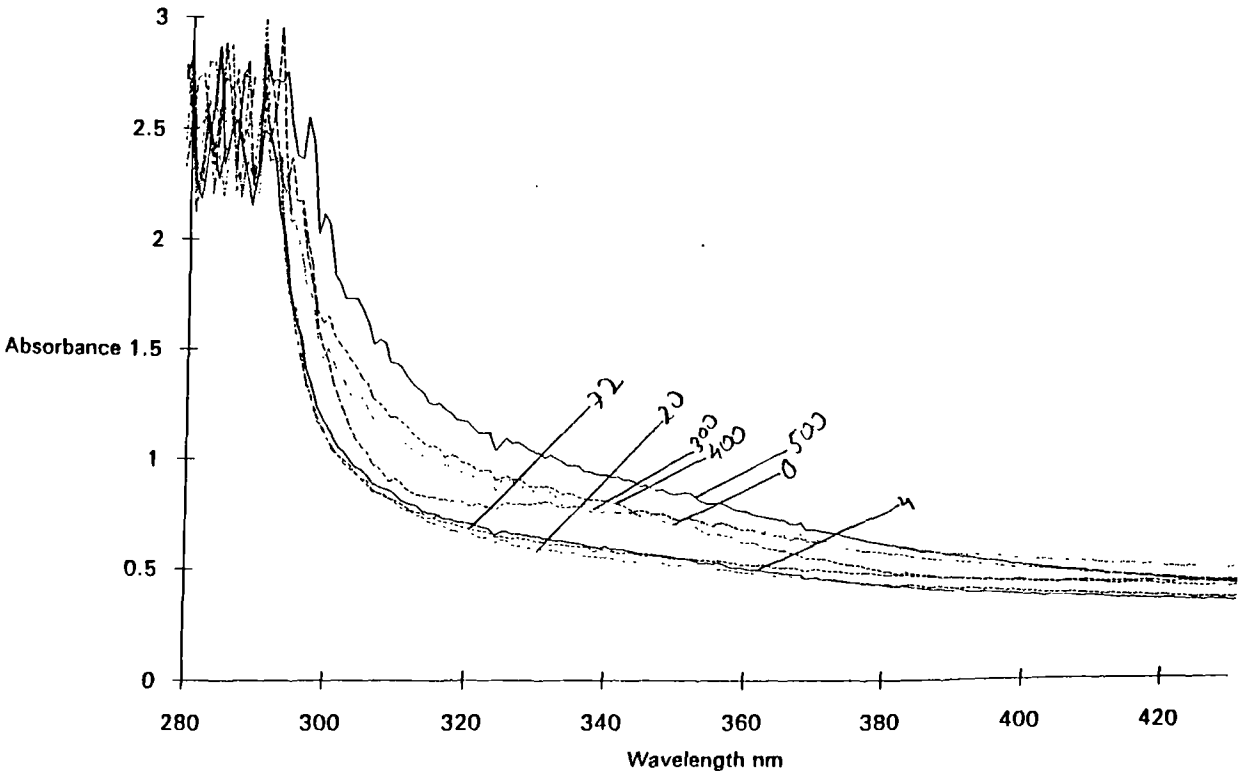


Fig 9.13

E9

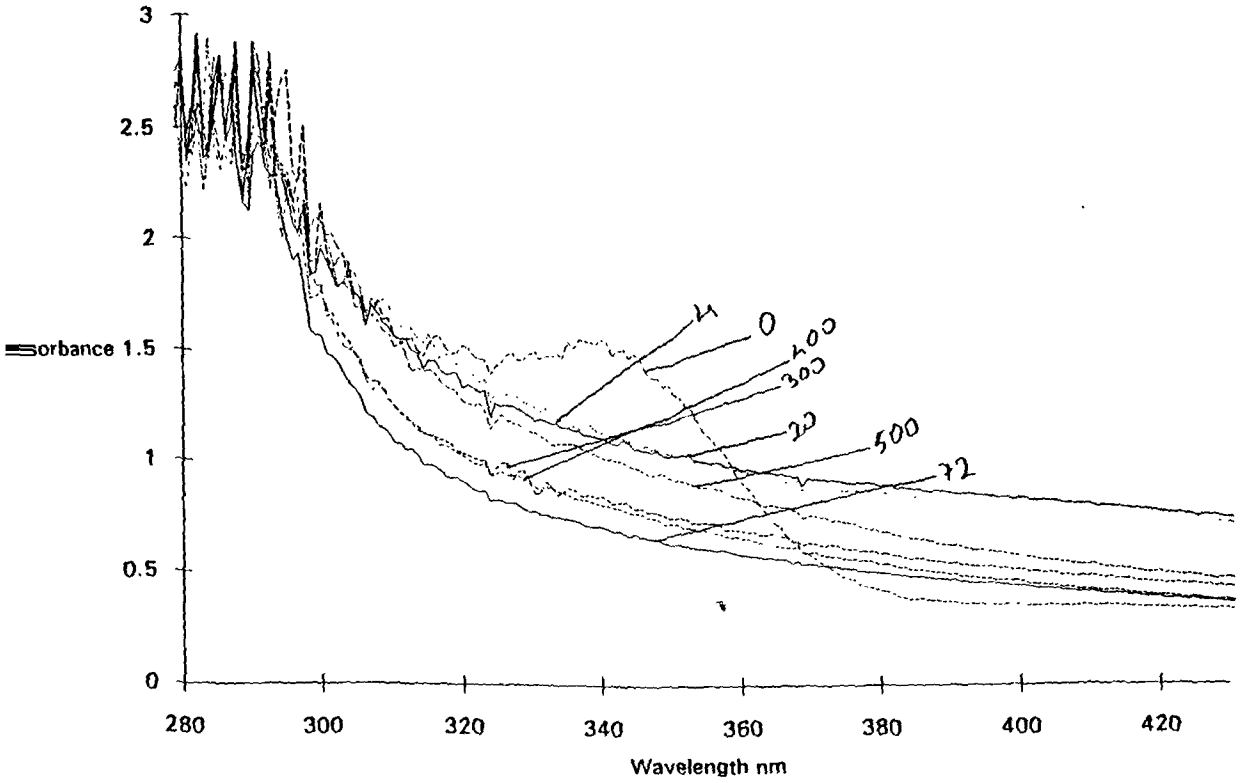


Fig 9.14

E10

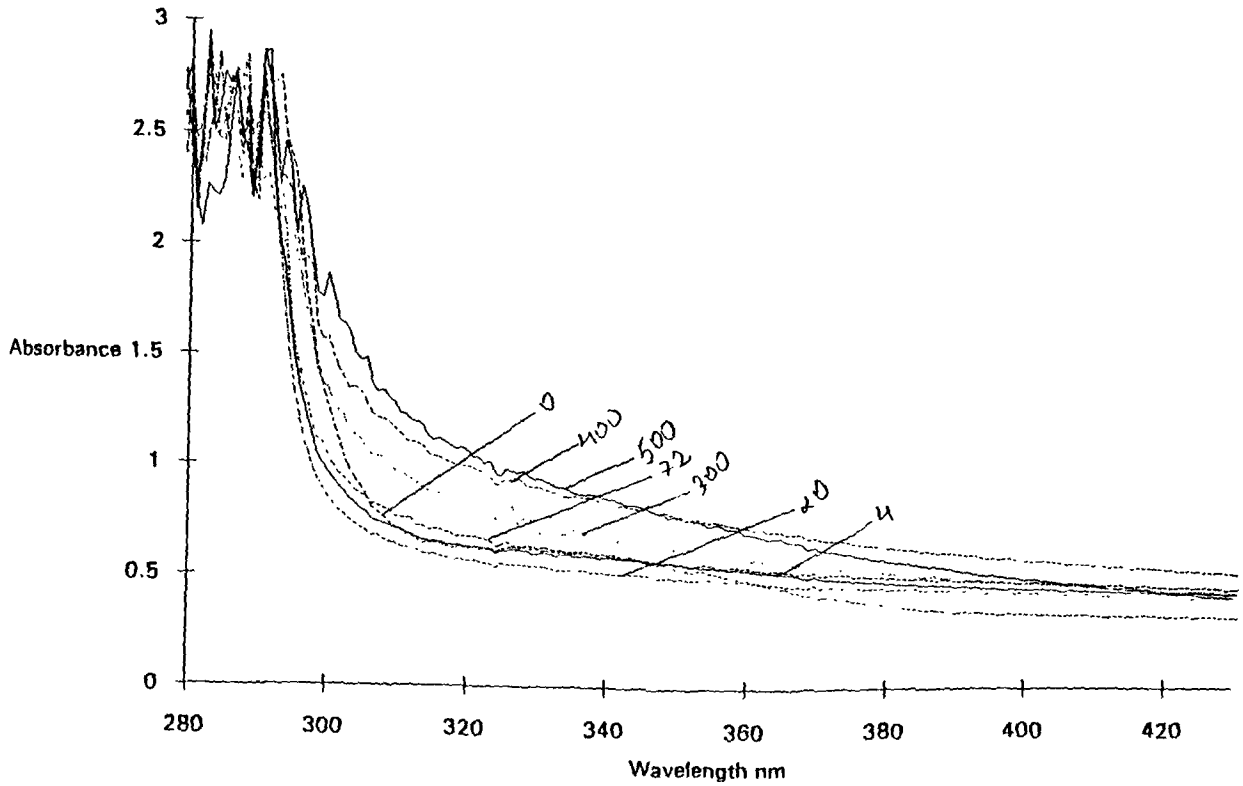


Fig 9.15

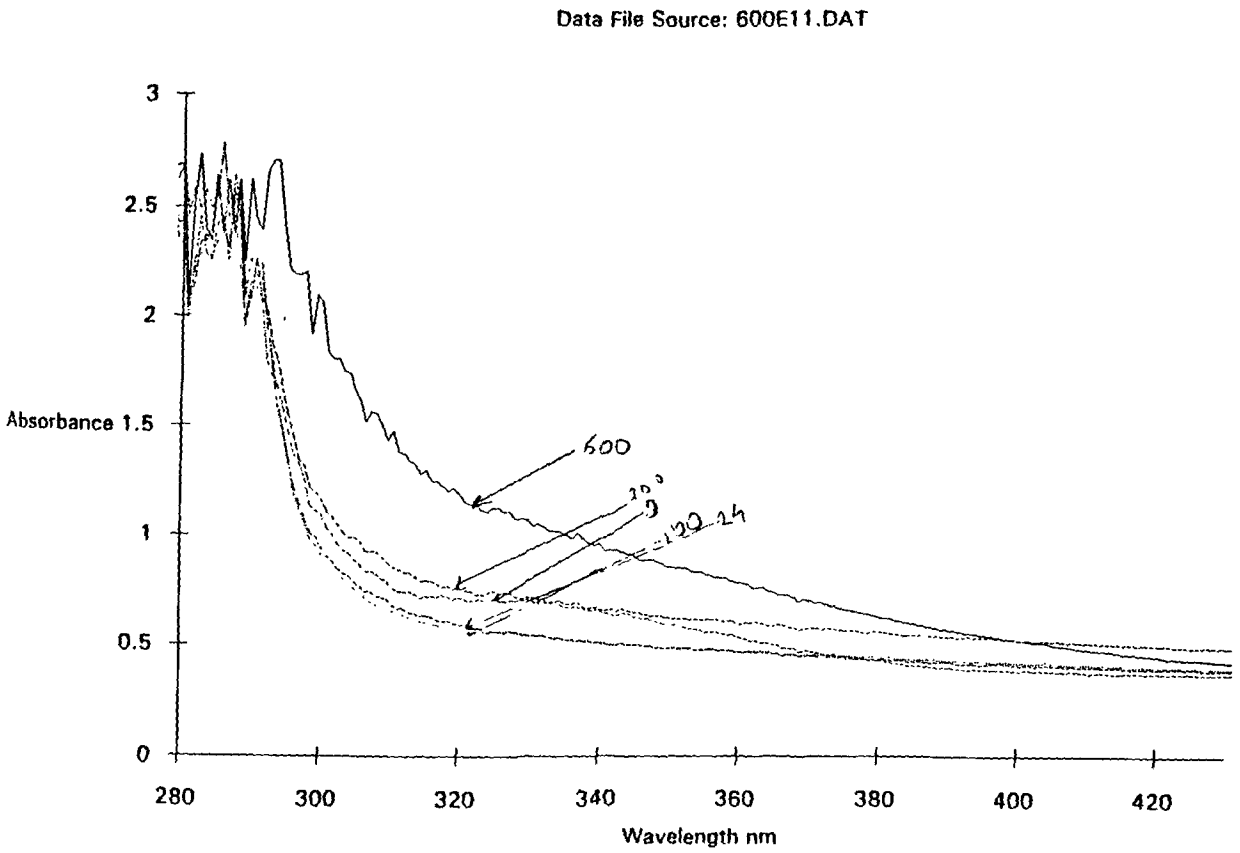

Data File Source: 600E11.DAT
Absorbance
3
2.5
2
1.5
1
0.5
0
280
300
320
340
360
380
400
420
Wavelength nm
600
120
24

Fig 9.16

Diarylketone triplet states are efficiently quenched by secondary and tertiary amines containing at least one hydrogen atom α to the nitrogen [30-34]. A charge transfer exciplex between the excited ketone and the amine forms first. Electron transfer to the excited triplet produces a radical ion pair, which immediately undergoes a proton transfer from the carbon α to nitrogen to the oxygen of the ketyl radical anion Fig 9.18

The acidity of the α-protons in amines is greatly enhanced after one electron oxidation of the nitrogen [32] so that a very fast proton transfer takes place which efficiently competes with back electron transfer.

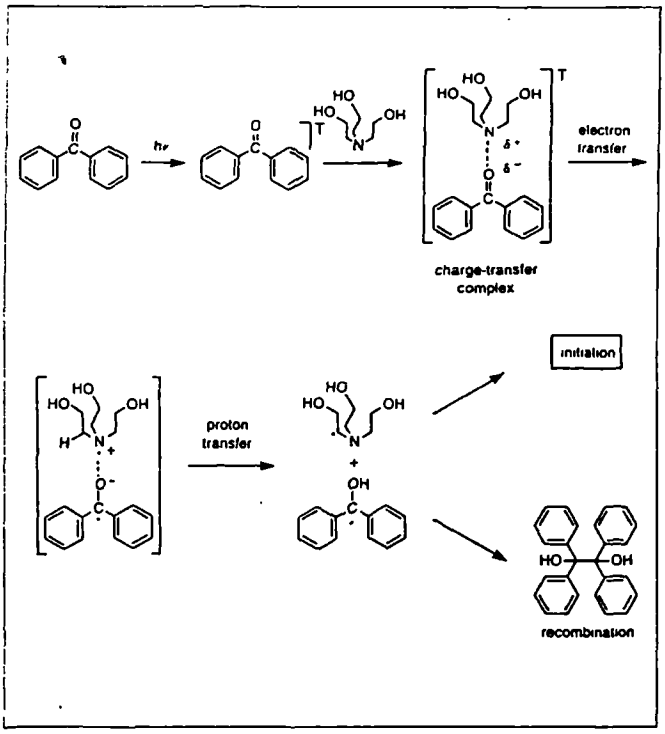
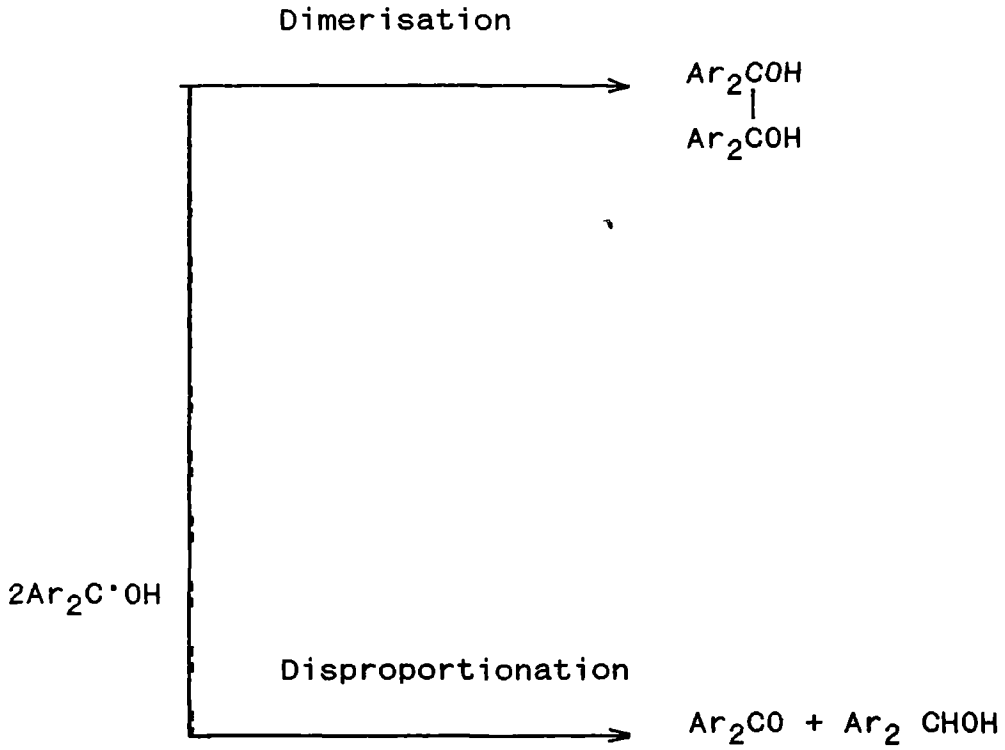


Fig 9.18

Due to steric bulk and delocalisation, the ketyl radical is insufficiently reactive to initiate polymerisation. This intermediate may undergo dimerisation, disproportionation, or react with oxygen.



$$Ar_2C^{\cdot}OH + O_2 \longrightarrow Ar_2CO + HO_2^{\cdot}$$

The addition of amine serves to increase the cure rate of polymerisation and lower the substantial differences between through cure and surface cure (caused by oxygen inhibition). The hydroperoxides (POOH) that accumulate during propagation will sensitise the photodegradation of the coating. The auto-oxidation of the growing polymer chain ultimately leads to

chain depolymerisation (chain scission [35]) which will occur at the "weak link" of the chain, i.e. a peroxide or ether link. The changes in the polymer structure arising by this mechanism, with concomitant crosslinking, will cause changes in the physical properties of the polymer such as embrittlement, colour, flexibility, hardness and so on. In this study, the different formulations which contain different aminoalcohols as a synergist were tested to determine the changes of their physical properties. Hardness and gloss changes on the film surfaces were monitored. Figs 9.19 ,20 and 21, display the pendulum hardness (in seconds) results against Q-UV weathering exposure. During the first 4 hours the pendulum damping times increased indicating that the coating became harder on weathering.

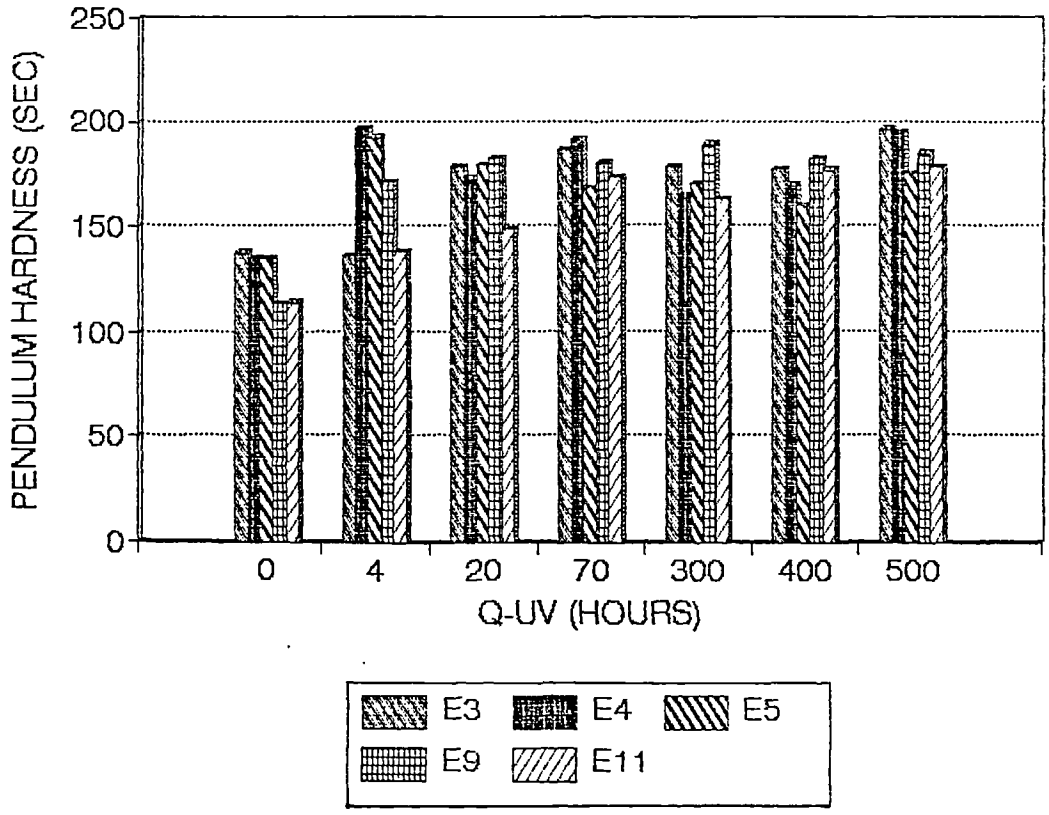


Fig 9.19 Pendulum hardness of UV cured samples with weathering

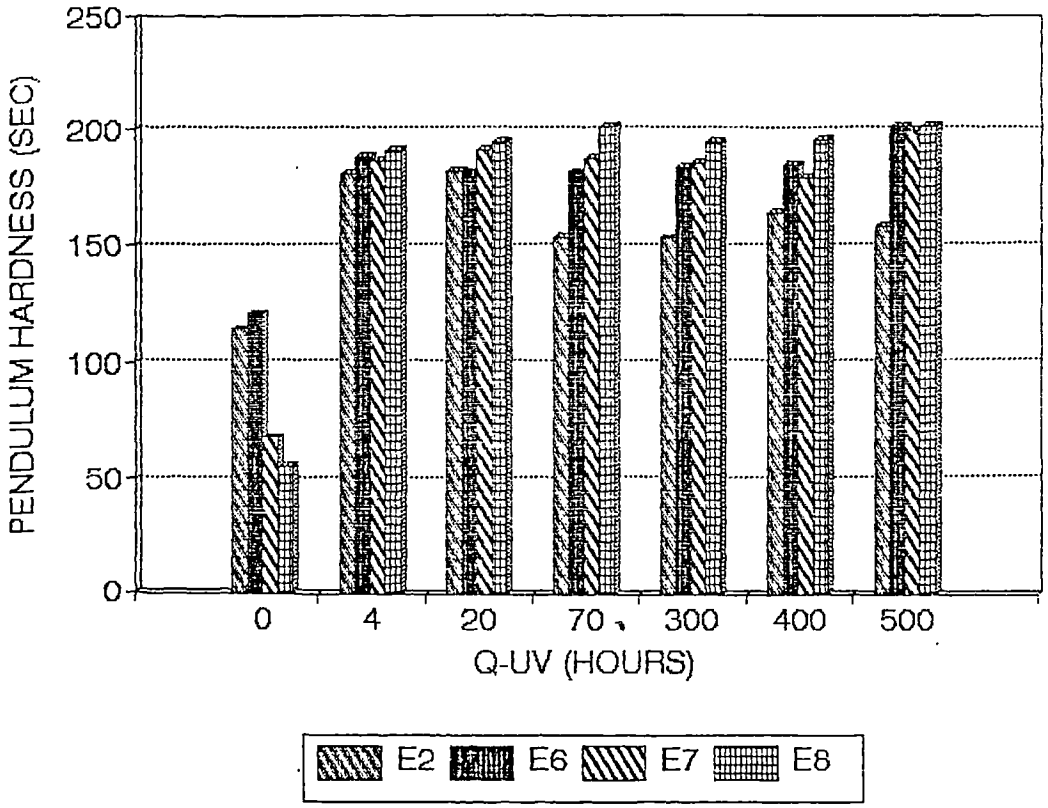


Fig 9.20 Pendulum hardness of UV cured samples with weathering

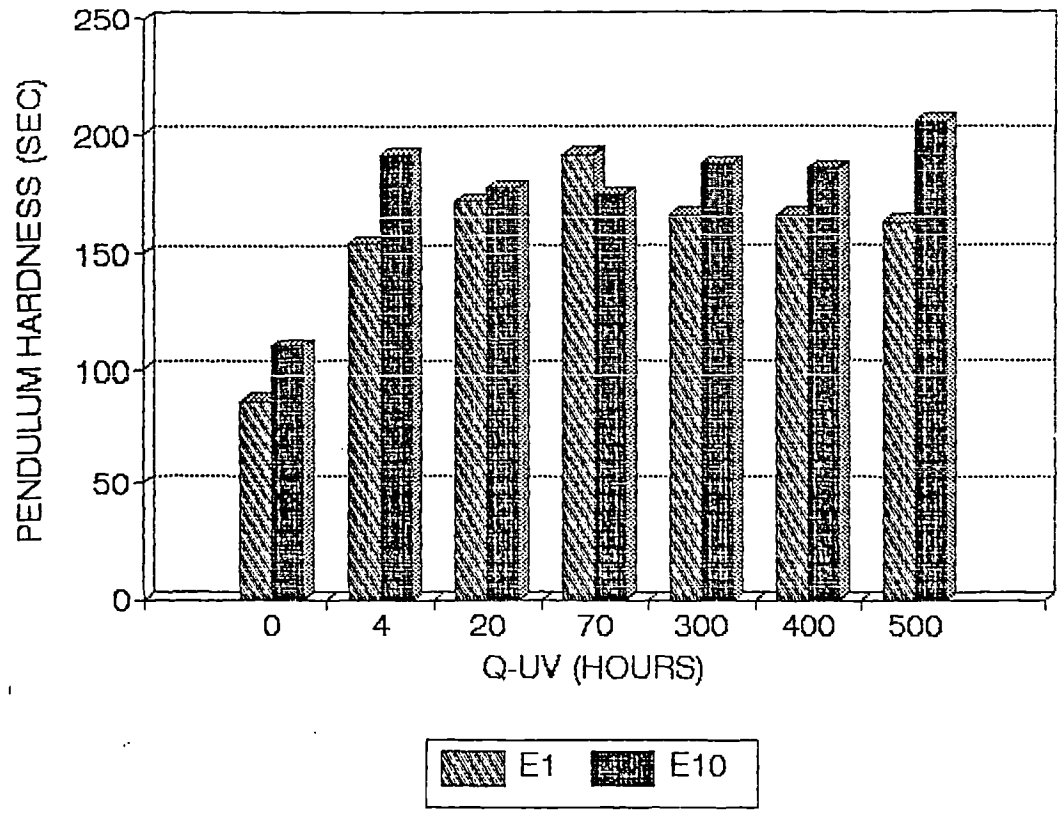


Fig 9.21 Pendulum hardness of UV cured samples with weathering

Figs 9.22, 23 and 24 display the gloss measurements (60^{o}) against Q-UV exposure time for the UV cured systems.

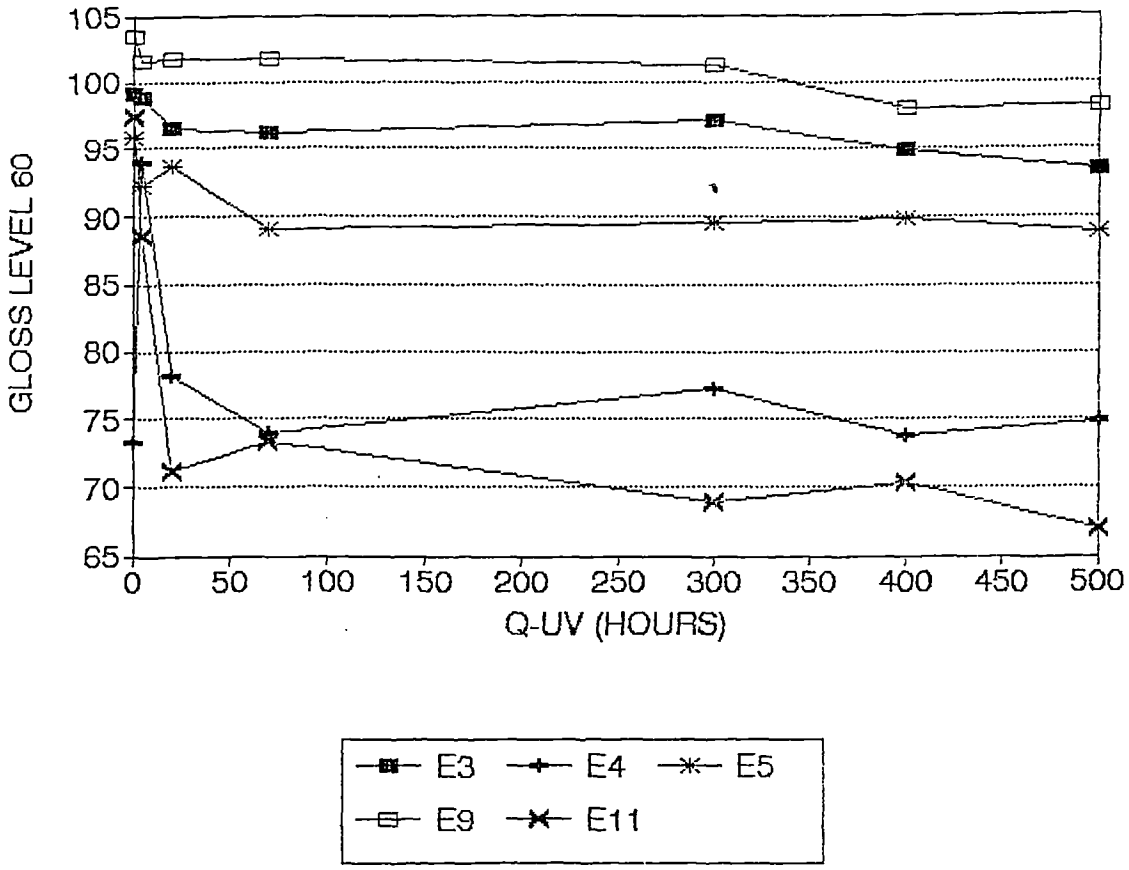


Fig 9.22 Gloss levels (60^{o}) of UV-cured samples

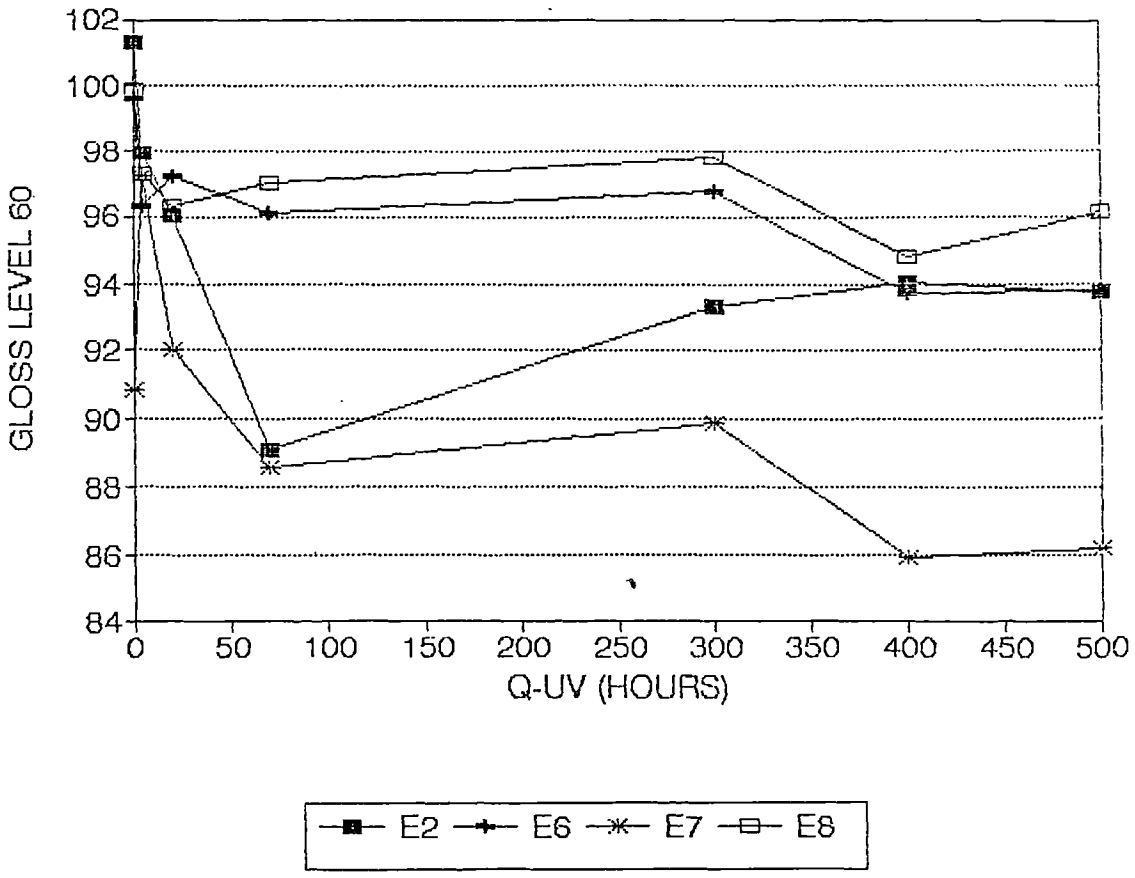


Fig 9.23 Gloss levels (60°) of UV-cured samples

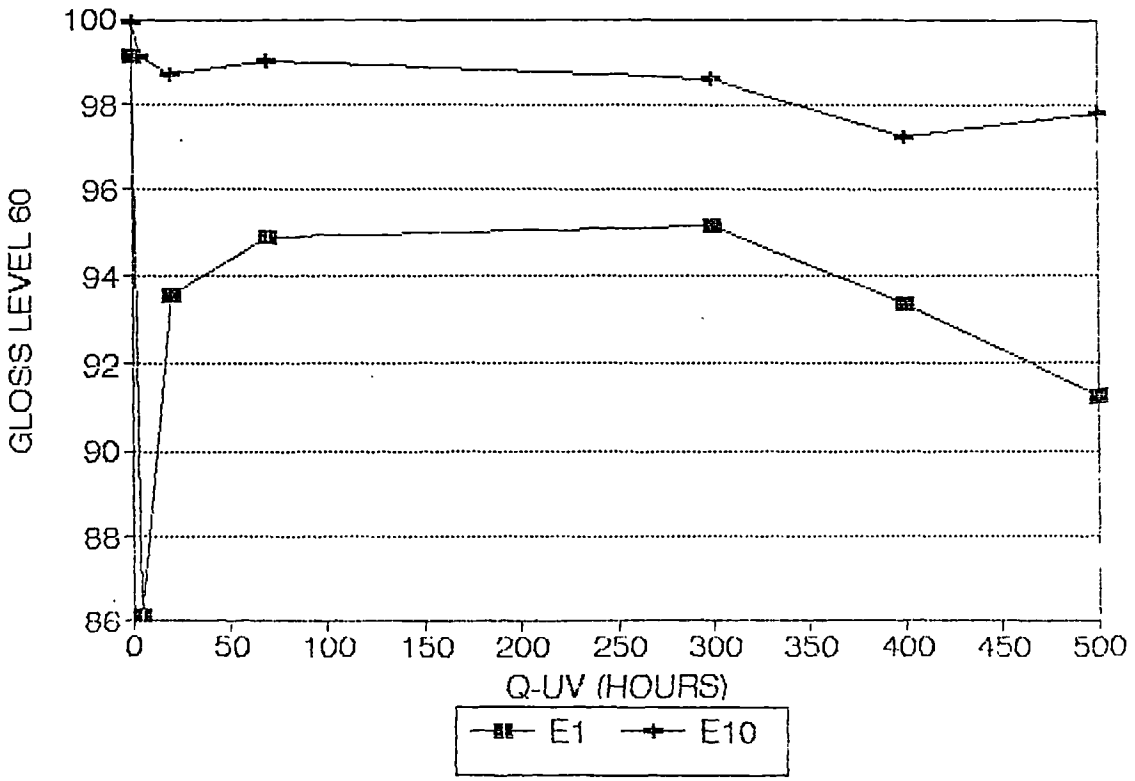


Fig 9.24 Gloss levels (60°) of UV-cured samples

Gloss levels (60^{o}) of all samples increased during 4 hours of weathering. When weathering was prolonged to 500 hours, it was observed that the gloss levels decreased, this is probably due to a change in the film thickness during Q-UV exposure. The rapid loss of gloss was observed for the samples: E4, E7 and E11.

All the other samples showed a steady but much slower decrease in gloss level on long term Q-UV exposure.

The yellowing characteristics of the formulations containing amino alcohols fall into three main classes:

(i) Extensive yellowing in the early irradiation period followed by an extensive period over which there is a little change in the level of yellowing,

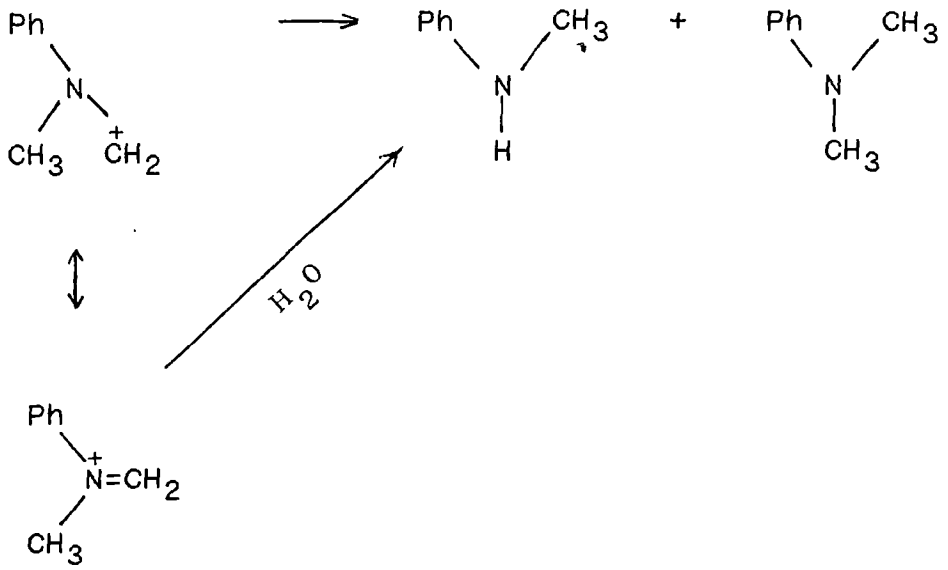
(ii) Extensive yellowing during the early irradiation period followed by bleaching and then a third period where either a small amount of yellowing occurs or there is a slight increase in the degree of yellowing, and

(iii) Yellowing rapidly occurs during the initial period, but not to a large extent and then this is followed by a slight increase in yellowing over an extensive irradiation period. When an amine is omitted from the formulation, the cured coating undergoes initial rapid yellowing to a small degree and then undergoes further yellowing at a much lower rate as irradiation is continued.

Although the yellowing process encountered in the aging of natural and synthetic polymers is far from being well understood, it is instructive to see if there are some structural features in the amino alcohols which account for how

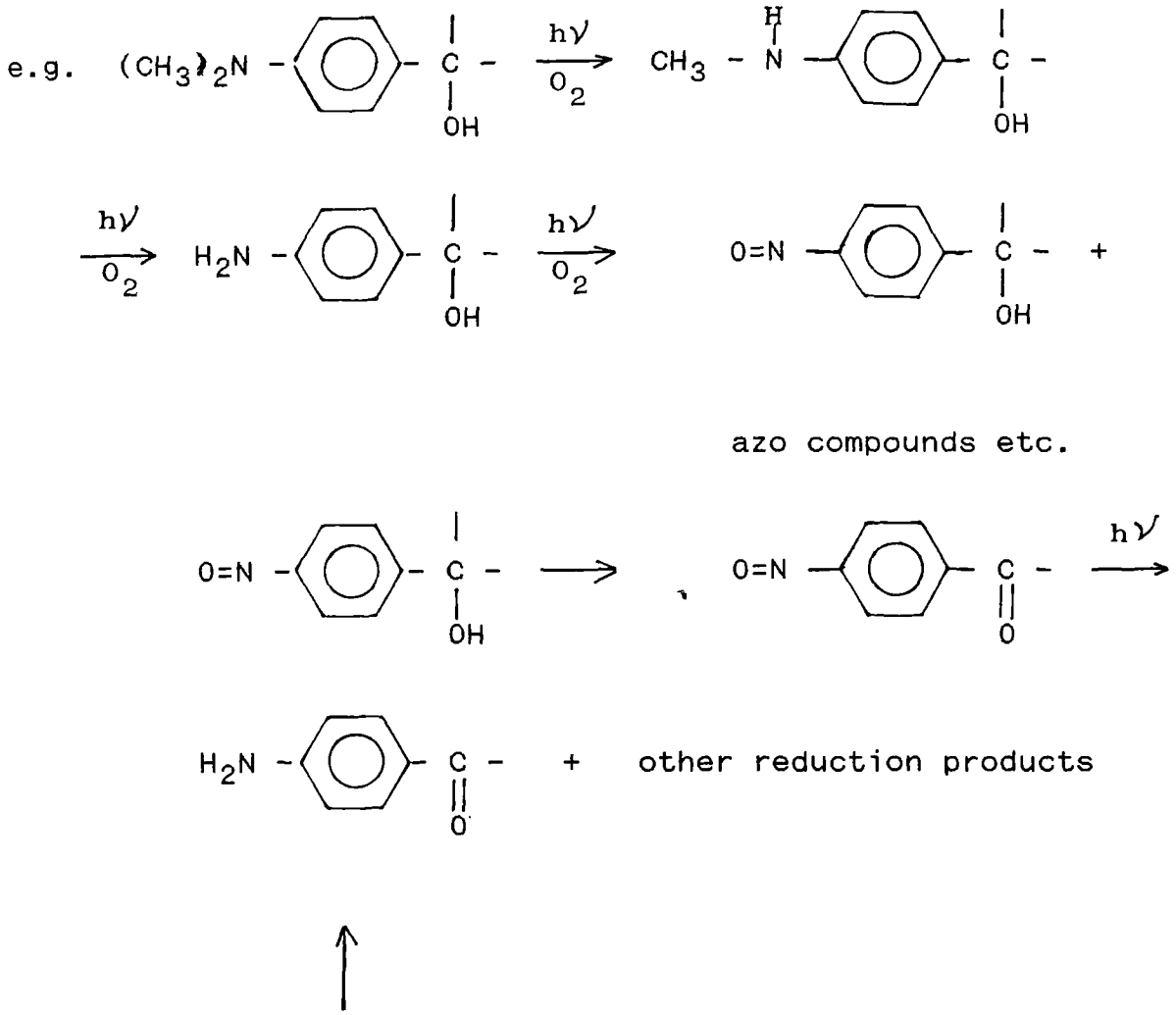
these materials are affecting colour changes in the coating.

Concerning the first class of yellowing behaviour, it can be seen that only E2 falls into this class. From earlier work it is known that E2 fragments on reaction with electronically excited acceptors to give a variety of products derived from the aminoalkyl radical (1).



Demethylation occurs and this process may well be enhanced by the presence of oxygen. The formation of a secondary aromatic amine opens up the possibility of formation of a range of coloured compounds in addition to further demethylation to give aniline (3) which can similarly give a plethora of coloured products. Thus the behaviour of E2 is reminiscent of what is observed when aromatic primary and secondary amines undergo oxidation. Amino alcohols which exhibit the second

class of photoyellowing include E4 and E9, both of which are substituted dimethylanilines i.e. they are structurally closely related to E2. These two amino alcohols lead to initial severe yellowing but on further irradiation bleaching occurs. Why should E4 and E9 behave differently to E2? For both E4 and E9 there is the possibility, like E2, of oxidising N-methyl groups but additionally there is the possibility of oxidation at carbon. In the case of E9 an aminobenzaldehyde may be formed by fragmentation or like E10 it may be oxidised to an aminoacetophenone. Aromatic amines carrying an electron withdrawing group seem to undergo little photoyellowing which is what has been observed for the synergist - 4-ethyl-dimethyl-aminobenzoate. The electron withdrawing group will reduce the propensity (2) for oxidation at nitrogen by raising the ionisation potential of the amine. Thus for E4 and E9 there is the possibility of rapid initial oxidation of the N-methyl groups giving a secondary and ultimately a primary aromatic amine. Further oxidation at nitrogen will become less probable following oxidation at carbon. Once the potential for oxidation at nitrogen has been reduced there is the possibility of photoreduction of the coloured chromophores (e.g. azo or nitroso compounds) with visible light and the reduction products will not be readily oxidised due to the presence of the withdrawing group.



Relatively stable towards photo-oxidation

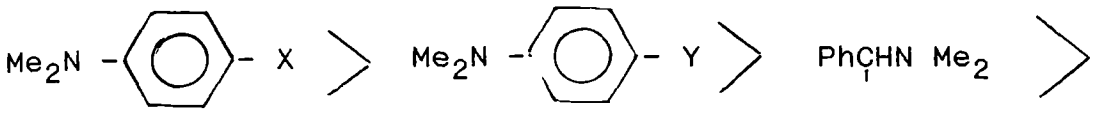
The only other amino alcohol to exhibit the second class of colouration behaviour is E5 which carries a morpholino substituent at the aromatic ring. It is likely that this amine undergoes little oxidation since it is known that N-substituted morpholines are relatively unreactive in electron transfer reactions (probably due to a high ionisation potential. E5 is however a substituted NN-dimethylbenzylamine and the N-methyl groups will undergo ready oxidation. Highly

coloured products are formed on oxidation of aliphatic amines due to the formation of Schiff bases and enamines together with their coloured oxidation products.

All the other amino alcohols and 1,2-diaminoethane exhibit the class (iii) type of colouration and lead to yellowing of the films which after 500 hours is no more extensive than that observed for the resin cured in the absence of amine. For all the amino alcohols in this class the amine component is either a morpholine or piperidine, both of which participate far less readily in electron transfer reactions (and hence probably oxidation processes) than dimethylamino groups. Thus it would seem that E6, E7, E8, E9 and E11 play a minor part in the yellowing process.

The behaviour of N-methyldiethanolamine is rather interesting in that its behaviour is similar to the other amines in this class. Thus, the N-methyl group does not appear to have a particularly profound effect.

To summarise, the propensity for amines to promote yellowing is the following:



X = H or electron donating group

Y = electron acceptor group

The question has to be asked - does the yellowing affect the physical properties of the films? A good indication of the extent of crosslinking in a surface coating can be obtained by measuring pendulum hardness. From the figures it can be seen that little distinction can be drawn between the films cured with the various amino alcohols. In the early stages of weathering there is an increase in pendulum hardness indicating that crosslinking is taking place. This is probably occurring via residual acrylate groups in addition to photo reactions of the residual benzophenone. After 20 hours of weathering most of the films - (all the films) are exhibiting a similar pendulum hardness.

EXPERIMENTAL

Formulation

Each of the UV cured free radical systems was formulated with 3% of benzophenone and 3% of aminoalcohols or amine (NMDEA) and 47% of epoxyacrylate (Craynor CN104) 47% of tripropylene-glycoldiacrylate (TPGDA).

Materials

All the aminoalcohols were prepared according to the methods given in Chapter 2. N-Methyldiethanolamine and benzophenone were obtained from Aldrich Chemical Company. Epoxyacrylate (Craynor CN104) and tripropylene plycol-diacrylate (TPGDA) were obtained from Cray Valley.

Substrate and Substrate Preparation

Chromated aluminium panels were prepared by rubbing down the panels with silicon carbide waterproof paper (220 grade), followed by degreasing in xylene. All films were laid down by a number 3k-bar (24μ).

Curing Conditions

Cure was achieved by using the Fusion System and all samples were irradiated with a 300 Watt/inch "H" lamp at a conveyor belt speed of 5m/min. Cure was assessed by a mechanical thumb.

Weathering Programme

The Q-UV cycle involved 4 hours irradiation with UV-A340 lamps, followed by 4 hours condensation repeated continuously.

Yellowing Index

The standard test method ASTM-E313-73 was used to measure the yellowing indices. This test method yields numbers that correlate with visual ratings of yellowness and whiteness of certain white and near-white surfaces.

All yellowing indices were measured using a Spectrogard colormeter (Pacific scientific). Calculation of the yellowing indices used is shown in equation 1.

$$YI = 100\ (1 - B/G) \qquad (1)$$

$$YI = 100\ (1 - 0.847\ Z/Y)$$

where;

G : Green or luminous reflectance (in percent).

B : Blue reflectance (in percent), (equal to Z/1.18).

Y : CIE luminous reflectance (in percent); identical with G and R_d when illuminated is CIE source C.

YI: Yellowness or Yellowing Index.

To determine the yellowing indices, five readings were recorded for each sample and then the average of five were calculated.

UV/visible spectra of each sample were recorded on a Philips PU 8740 UV/visible light scanning spectrophotomer.

Gloss

Gloss measurements were recorded using a Rhopoint laboratory gloss meter with a 60^{o} head.

Pendulum Hardness

Pendulum hardness results were assessed as mentioned in Chapter 5.

Personal Acknowledgment

I would like to thank Dr Eleanor Cockburn at the Paint Research Association for carrying out the physical test results presented in this thesis.

I am also grateful to Dr Richard Holman and Miss Jackie Crisp for their kind help and assistance.

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CHAPTER 10

DUAL CURE

Chapter 10. DUAL CURE

INTRODUCTION

UV-Curing Systems have proven their value for the printing and coating industries. A limitation, however, is the shrinkage occurring during the polymerisation leading to a lack of adhesion on certain non-porous substrates. The high crosslinking density of these systems often leads to the formation of a hard but rather brittle coating that is very difficult to bend or emboss.

The use of dual curing systems was proposed in order to overcome these problems. In these systems two types of functional groups are present, one sensitive to the radical curing reaction induced by UV radiation, generally acrylic double bonds, the other suitable reaction which aims via a different mechanism is: e.g. Acrylate-Cycloaddition, Acrylate-Rearrange-ment (Diazoketone), Epoxide (Vinyl ether + Rearrangement, Epoxide/Vinyl ether + Cycloaddition. In dual cure systems, the crosslinking of the system, leading to the final properties is achieved during the second step.

By proper choice of the type of chemical structure and the ratio between both types of functionalities, dual cure systems can perform like a pure UV-system without, however, the typical limitations of the UV technique.

The dual cure character of the system can be achieved by

incorporating both types of functionalities on one chemical structure or by mixing two products with different types of functionality together.

Systems which Crosslink by Cycloaddition Reactions

1. Cinnamates and Related Types as Pendant Groups

Polyvinylcinnamate is one of the best known examples of a material which becomes insoluble through a photocyclo-addition process. The reaction involves the activation of the cinnamate ester exocyclic C=C double bond. This excited chromophore then interacts with another cinnamate moiety in the ground state [2,3]. The results of the dimerisation of two units belonging to two different polymer chains is the formation of a cyclobutane ring between the chains as shown in Fig 10.1

The cinnamate moiety can readily be introduced as pendant groups into a number of polyhydroxylic preformed polymers such as polyvinylalcohols [4-7].

On the basis of the fact that cinnamic acid causes photodimerisation in the solid state, polyvinylcinnamate appeared to be a photosensitive polymer. It has been widely used as a photo-resist in printing and in the

production of electrical circuits. The polymer is usually prepared by the reaction of polyvinylalcohol and cinnamoylchloride.

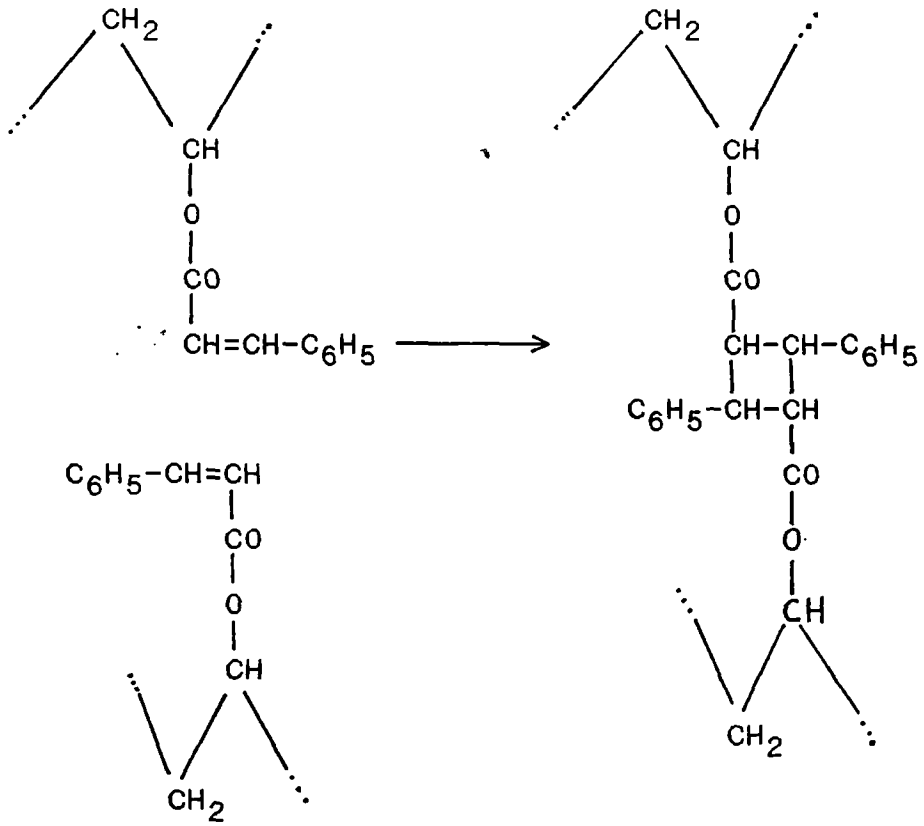
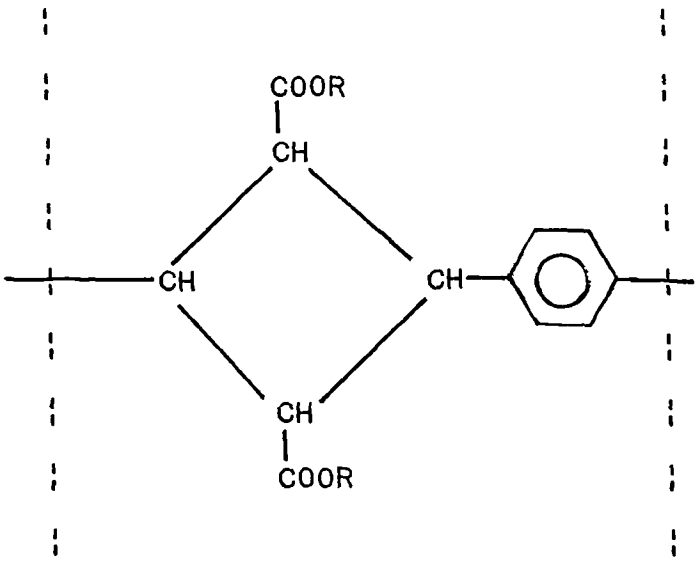


Fig 10.1 (2+2) Photocycloaddition of cinnamate ester units pendant polymer chains

2. Cinnamate-Like Groups in the Main Polymer Backbone

The light-sensitive groups are attached to the polymer backbone as pendant side-units as shown in Fig 10.1 Light-sensitive groups structurally related to the cinnamoyl chromophore can, however, also be introduced as integral parts of the polymer backbone. This has, for example been achieved by polycondensing 4-carboxycinnamic acid [8] or p-phenylenediacrylic acid [8-12] with diols to produce linear polyesters with photodimerisable groups along the main chains.

Novel high molecular weight linear polymers [A] have been prepared by irradiation of monomeric p-phenylene diacrylate derivatives in the crystalline state [13]. Polymer formation was due to repeated [2+2] cyclo-addition.



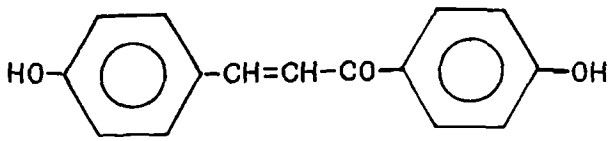
[A]

3. Chalcone-Type Units as Pendant Groups

As in the case of the cinnamates mentioned previously, chalcone-type groups also dimerise to form cyclobutane rings on UV irradiation. They can be introduced onto polymer chains as pendant groups in various ways to form photocrosslinkable polymers. Examples are; by the condensation of polyvinylacetphenone with benzaldehyde [14,15] by Friedel-Crafts' reaction of polystyrene with cinnamoyl chloride [16], by the addition of α-isocyanatobenzalacetophenone to polyvinylalcohol [17], or by the reaction of styrene-maleic anhydride copolymers with 4-methoxy-4'-(α-hydroxyethoxy)-chalcone [15,18,19].

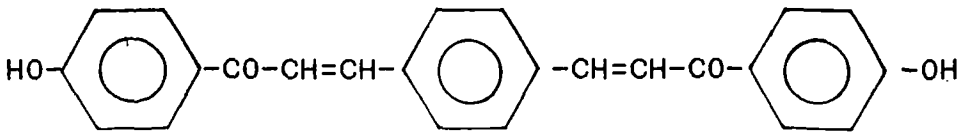
4. Chalcone-Type Groups in the Main Polymer Backbone

The ease of synthesis of chalcone-type compounds has led to extensive work on the synthesis of a large variety of photocrosslinkable polymers containing this functional group 4,4'-dihydroxychalcone [B]. This is obtained by the condensation of α-hydroxybenzaldehyde with α-hydroxy-acetophenone [20,24].



[B]

A different light-sensitive bisphenol [C] can be made by the condensation of terephthaldehyde with α-hydroxy-acetophenone.



[C]

Photocrosslinkable resins and polymers can be made from these light-sensitive bisphenols in a variety of ways [20-24,25,26,27,28].

UV-crosslinkable polymers containing up to 30% metal ions have been synthesised by reacting light-sensitive bisphenols with a di-acid chloride and an organometal dihalide [29] .

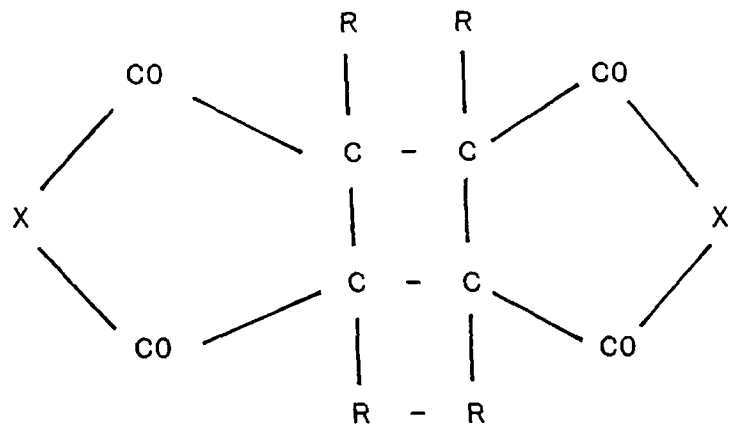
5. Coumarin Types

Coumarin has been shown to undergo (2+2) cycloaddition on UV irradiation, forming four isomeric dimers (two head-to-head and two head-to-tail). The product distribution is much influenced by factors such as monomer concentration, the nature of the reaction solvent, and whether triplet sensitiser is present [30]. The light sensitivity of the coumarin-functional polymer appears to be slightly lower than that of polyvinyl cinnamate [31].

The photosensitivity of the coumarin-functional polymers seems to be proportional to the mole fraction of the light-sensitive units present [39].

6. Maleic-Type Derivatives

The photocyclodimerisation of the anhydrides and various imides of maleic and dimethylmaleic acids, forming the corresponding cyclobutane derivatives [D] is well established, and proceeds whether the systems are sensitised or are irradiated directly [32,33,34].



[D]

A number of linear polymers have been prepared by UV-irradiation of various bismaleimides [35-37]. A large number of photocross-linkable maleic-type resins have also been described, most of these being polymers containing pendant-substituted maleimide units [38].

Types of "Dual Functionality" System

a. Dual Functionality Resins. In principle, many possibilities exist for the synthesis of cross-linkable resins containing both light-sensitive units and heat-activated groups. Dual functionality epoxy resins with attractive technical properties have, for example, been prepared by advancement of the diglycidyl ethers of chalcone-type bisphenols with Bisphenol A or with 5,5-dialkylhydantoins [39]

Another technique involves the introduction of light sensitive groups at suitable positions on epoxy resin molecules [39]. . Other possibilities exist, including reaction of the epoxy groups of a resin with a material which contains both carboxylic acid units and photopolymerisable groups.

Stepwise cure can be attained with systems comprising:-

i) a compound containing both an epoxy group as a (methyl)acrylate ester unit,

ii) a catalyst capable of causing photopolymerisation of the unsaturated moiety,

iii) a heat activated hardener to cure the epoxy groups at the final stage.

b) Mixtures of Materials of Different Functionalities

Much of the work in this area has involved epoxy resins as the heat-cross-linkable components, but various other resins can alo be employed.

As a very simple example, systems consisting of:-

(i) a conventional epoxy resin,

(ii) a light-polymerisable component such as an acrylic or methacrylic ester,

(iii) a photoinitiator,

(iv) a heat-activated epoxy hardener such as dicyanamide may be mentioned.

Initial UV-exposure leads to photopolymerisation of the unsaturated component, thus changing the system from its original liquid state into a more viscous (or solid) material. The epoxy resin and its hardener become entrapped in the photopolymerised network at this stage.

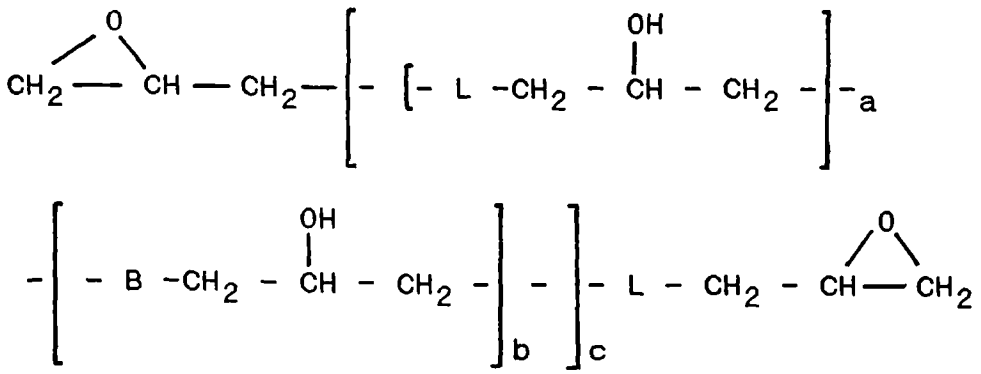
c) Resins Containing a Group at which both Photo-polymerisation and Thermally Induced Reaction Can Occur.

A number of systems have been described in which the resin molecule contains a group that is capable of both light- and heat-induced reactions and two different catalysts are present - one being light-sensitive, the other heat sensitive. A typical example of such a system [39] contains Bisphenol A diglycidyl ether, diphenylamine-4-diazonium tetrafluoroborate and dicyandiamide.

Applications of Two-Step Cure

"Dual functionality" resins capable of stepwise, sequential crosslinking as described previously have a number of important technical advantages.

The resins (E) developed for the manufacture of multilayer printed circuits.



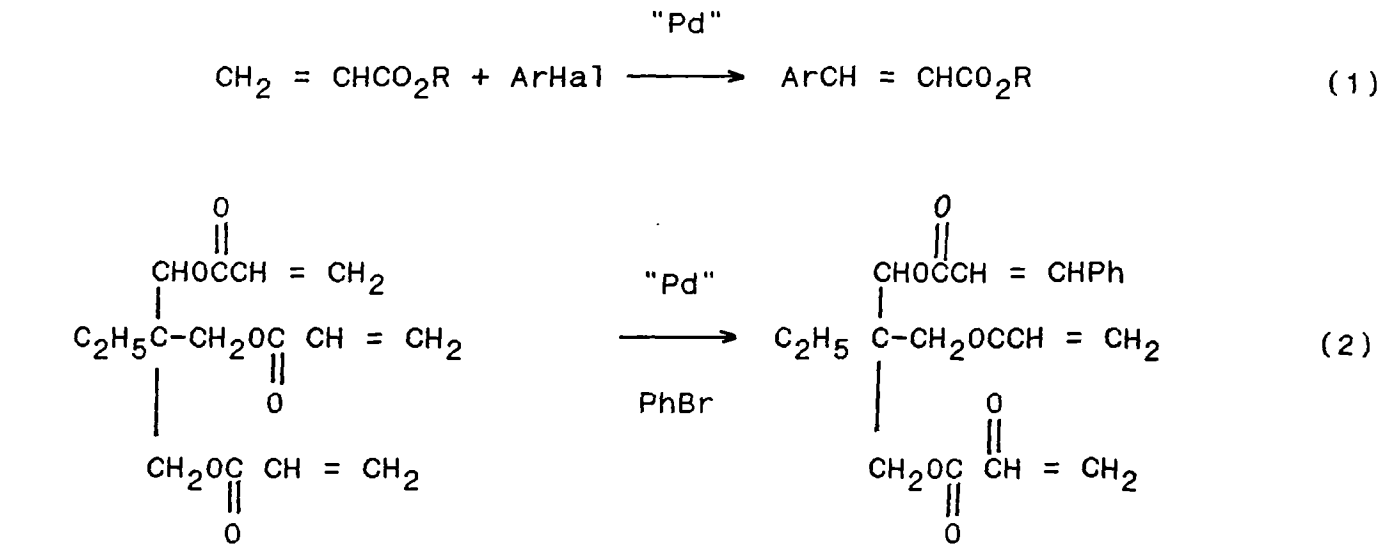
(E)

In these resins, light-sensitive groups, L, are built into an epoxy resin molecule which also contains bisphenol or other residues, B. On irradiation, the L groups are photocross-linked, so that the resin becomes insoluble in the developer. After the imaging procedure, the resin can be cross-linked further by heating with a conventional epoxy hardener (E).

The potential advantages offered by this process include faster production speeds, elimination of solvent, and savings in energy. In theory, there are many "dual functional" chemical compositions that can be applied in such a process. Similar principles can also be used in a variety of other applications; these include the solventless preparation of adhesive films, the production of sheet materials based on butadiene resins , coils , liquid crystal display cells, and various coating processes.

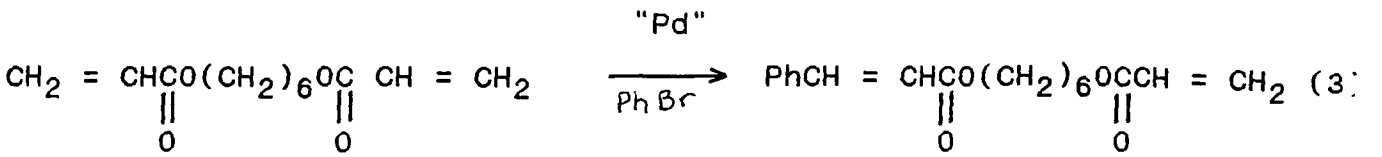
RESULTS AND DISCUSSION

Some mixed acrylate-cinnamate systems were prepared to investigate a new dual cure system. In this study; trimethylolpropanetriacrylate, 1,6-hexanedioldiacrylate, methylmethacrylate, 2-hydroxyethyl diacrylate and pentaerythritoltriacrylate were arylated via a novel route which has a wide applicability. As shown in Schemes.1,2 and 3.



$$CH_2 = CHCO_2R + ArHal \xrightarrow{\text{"Pd"}} ArCH = CHCO_2R \qquad (1)$$

$$C_2H_5C(CH_2OCCH=CH_2)_3 \xrightarrow[\text{PhBr}]{\text{"Pd"}} C_2H_5C(CH_2OCCH=CHPh)(CH_2OCCH=CH_2)_2 \qquad (2)$$



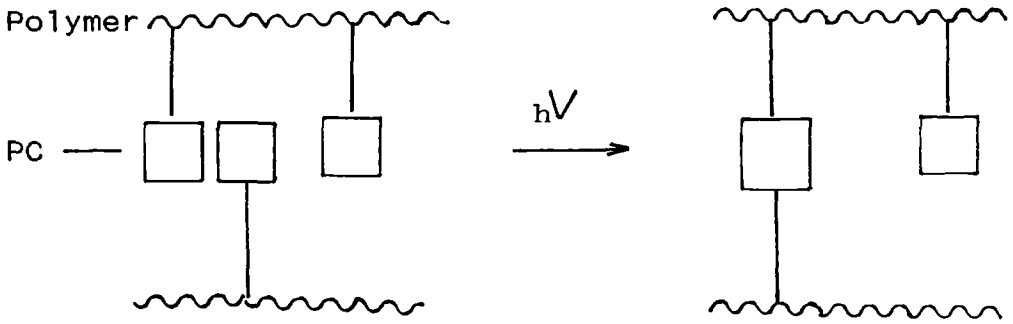
$$CH_2 = CHCO(CH_2)_6OCCH=CH_2 \xrightarrow[\text{PhBr}]{\text{"Pd"}} PhCH = CHCO(CH_2)_6OCCH=CH_2 \qquad (3)$$

The same method was employed to prepare arylated-PETA and for the other acrylates

These systems possess two functional groups, one which is sensitive to the radical curing induced by UV radiation and the other one suitable to react by a different mechanism. In this study; Acrylate-Cycloaddition systems were investigated. These systems need to be able to operate at two wavelengths and ideally in the presence of Type I photoinitiator.

$$PI \xrightarrow{h\nu_1} Radicals$$

$$Radicals + Acrylate \longrightarrow Polymer$$



Where PC is Photocrosslinkable group e.g. cinnamate, chalcone and styrylpyridinium.

Fig 10.2

As shown in Fig 10.2, it was proposed to cure the acrylate by a free radical mechanism and then alter the film properties e.g. by making it harder, by crosslinking the cinnamate residues via a (2+2) cycloaddition reaction.

A simple mixture of acrylates and cinnamates could be used but film performance would be poor since the two systems will not be covalently linked in any way.

Photocyclo-addition reactions may involve either the singlet or triplet excited states of the chromophore. If a triplet sensitiser is present the cyclo-addition via the triplet excited states predominates(Fig 10.3) [39]

$$M^0 \longrightarrow M^1$$

$$M^1 + M^0 \longrightarrow \text{dimers or crosslinks}$$

$$M^1 \xrightarrow{ISC} M^3$$

$$S \xrightarrow{h\nu} S^1 \xrightarrow{ISC} S^3$$

$$S^3 + M^0 \longrightarrow M^3$$

$$M^3 + M^0 \longrightarrow \text{dimers or crosslinks}$$

Fig 10.3

Where:

M : Monomer

S : Sensitiser

0, 1 and 3 refer to the relevant ground, singlet and triplet states, respectively.

ISC : Intersystem crossing from excited singlet state to triplet state.

It has been deduced that the lowest triplet state of the cinnamate group is at about 57 kcal/mole. For a sensitiser to be efficient, it must have a very high extinction coefficient at the wavelength of the light used for irradiation in order to absorb adequate light energy when present at a relatively low concentration in the substrate.

For a high population of sensitiser molecules to be maintained in the triplet state, the quantum yield of intersystem crossing (Φ_{ISC}) must also be high.

To obtain efficient energy transfer, the triplet lifetime must be reasonably long ($I_t > 10^{-2}$s) and the energy level of the triplet donor must be close to that of the acceptor.

It is known that cinnamate groups deactivate the Type II photoinitiators but this is not so for the Type I initiators since these have such short triplet lifetimes. From this basic knowledge, Type I initiators were chosen namely: Irg 651 (2,2-dimethoxy-2-phenyl-acetophenone) and Irg 907 (2-methyl-1-[4-(methylthiolphenyl]-2-morpholino-propan-2-one) to test arylated-acrylate systems and also N-methyldiethanolamine was used in some experiments.

The systems were tested using Colordry with a 100w/per.inch medium pressure mercury lamp. The results were obtained for slow belt speed with a number of passes to achieve tack-free cure.

The degree of cure for each film was measured arbitrarily using a hard rubber bulb. The film surface was rubbed firmly by rubber bulb. The substrate used was GNT paper (mentioned in Chapter 5). When determining the degree of cure during the experiments, cure quality was extremely poor. The number of passes was much higher than 30 which even at 30 is a sign of poor cure. It was observed that no polymerisation occurred during irradiation of samples.

Two other methods were employed to test the degree of cure; RTIR (Real Time Infrared Spectroscopy) as mentioned in detail in Chapter 4 , and IR Spectroscopy combined with Colordry.

When the second method was used, the samples were cured using Colordry and conversion percentage was determined by IR spectroscopy changing at 810 cm^{-1} peak. The RTIR and IR + Colordry spectra are shown in Figs.10.5-10.13

As can be readily seen, the conversion percentage is very low for arylated acrylates + initiators. Trimethylolpropane-triacrylate (TMPTA) itself gives a much higher rate of cure than arylated acrylates + initiator systems.

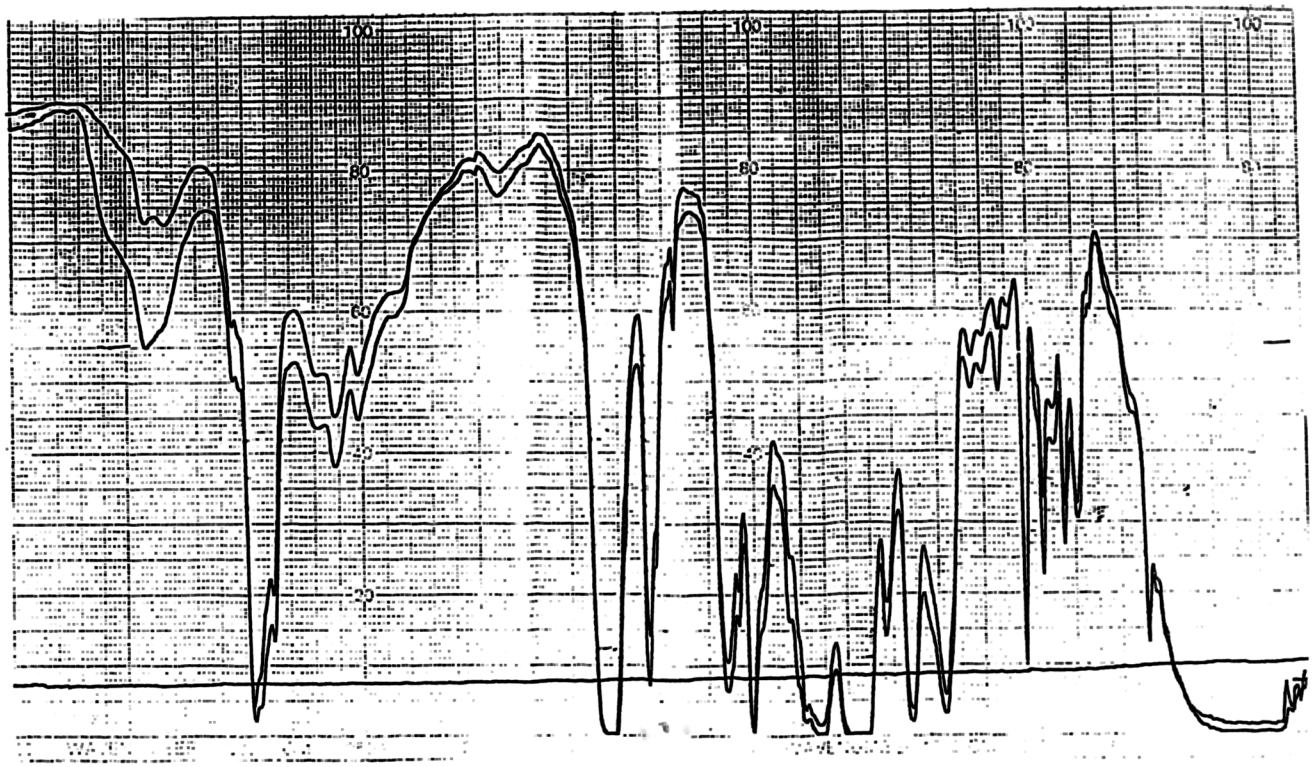


Fig 10.4 RTIR Spectrum of Cinnamoylated TMPTA + Irg 651

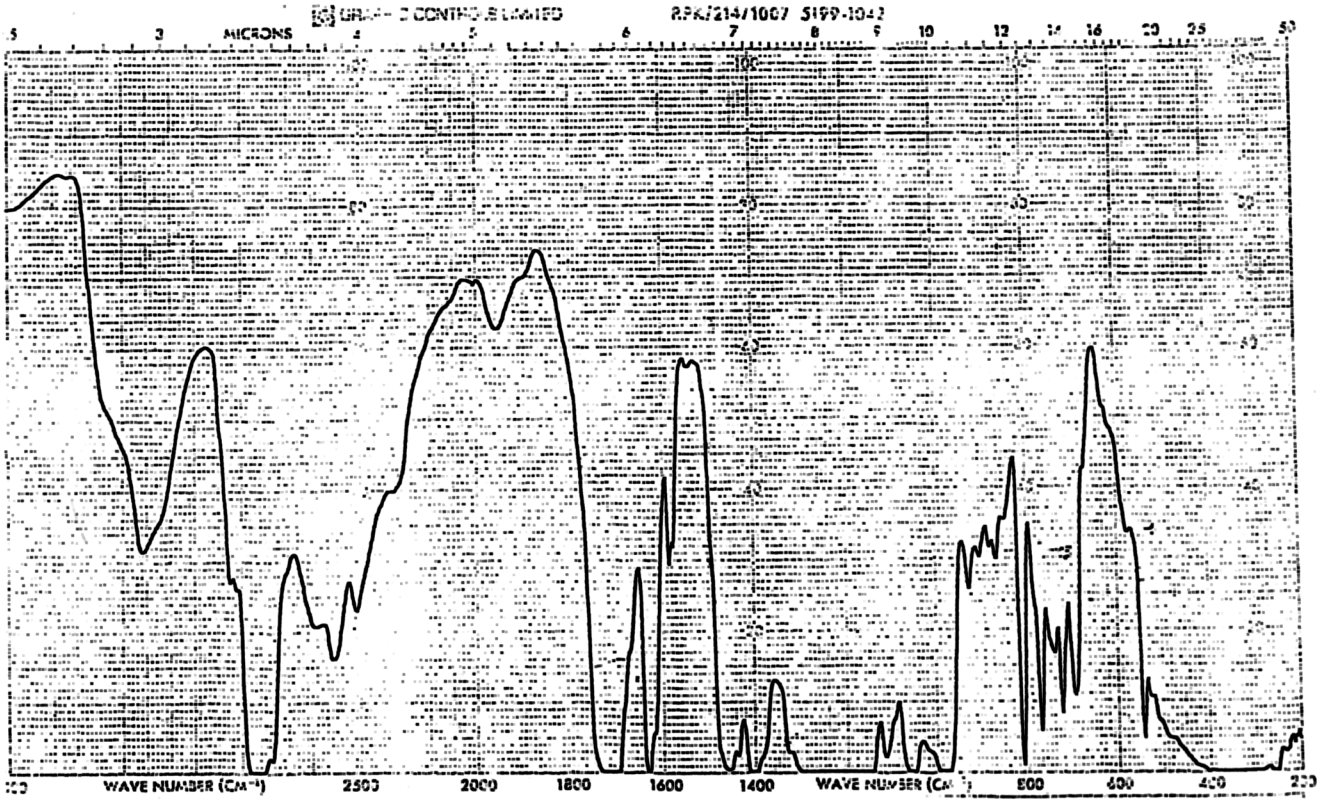


Fig 10.5 IR Spectrum of Cinnamoylated TMPTA + 2% of Irg 907 before irradiation

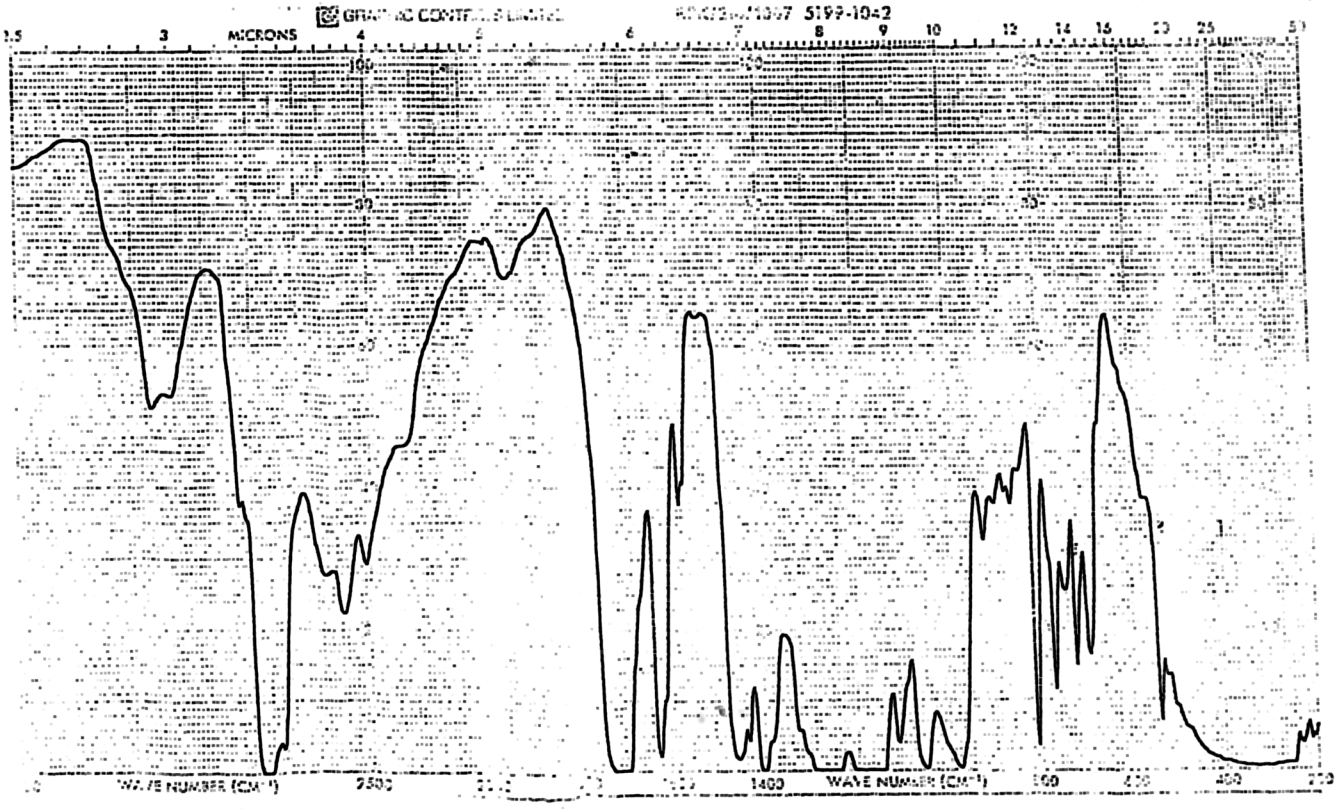


Fig 10.6 IR Spectrum of Cinnamoylated TMPTA + 2% of Irg 907 after 5 passes under Colordry

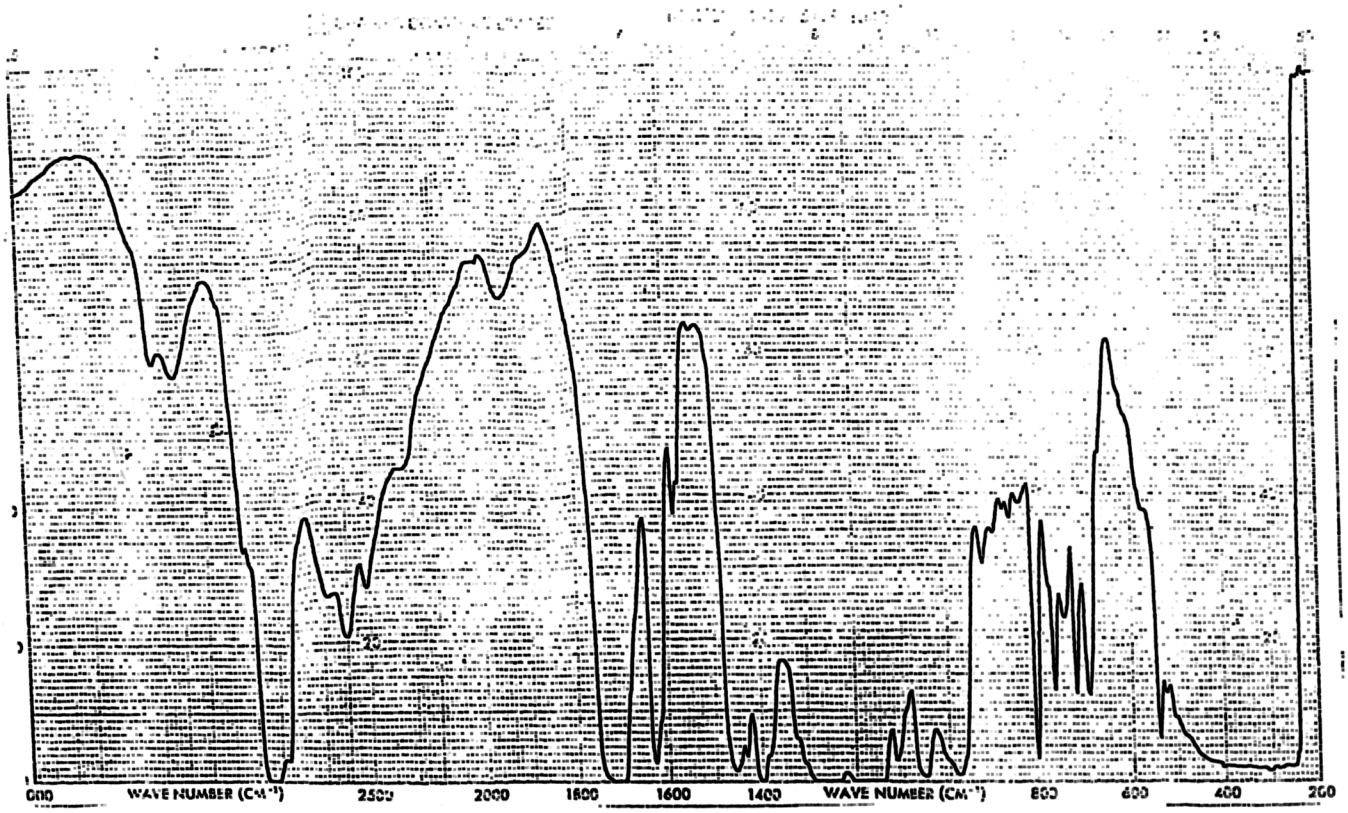


Fig 10.7 IR Spectrum of Cinnamoylated TMPTA + 2% of Irg 907 after 30 passes under Colordry

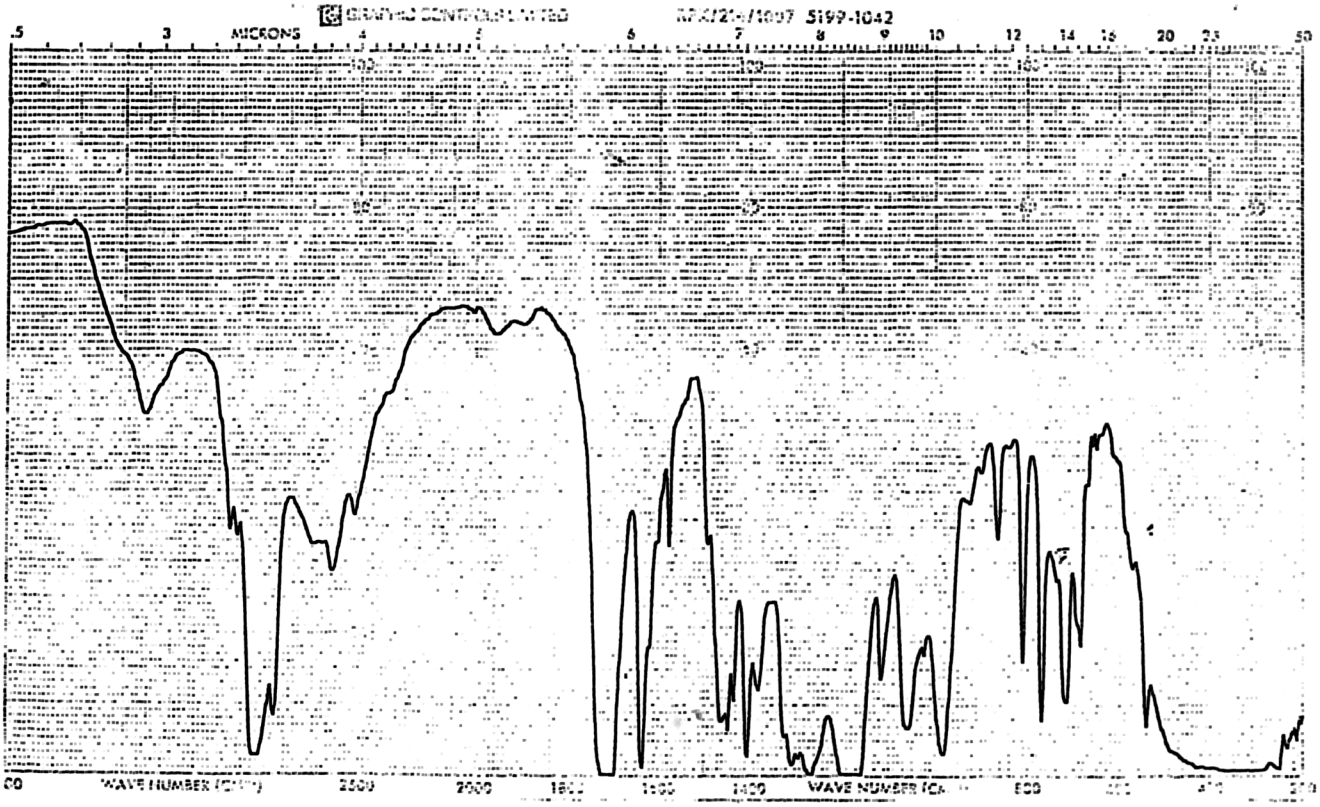


Fig 10.8 Before Irradiation of Cinnamoylated HDDA + Benzoylperoxide

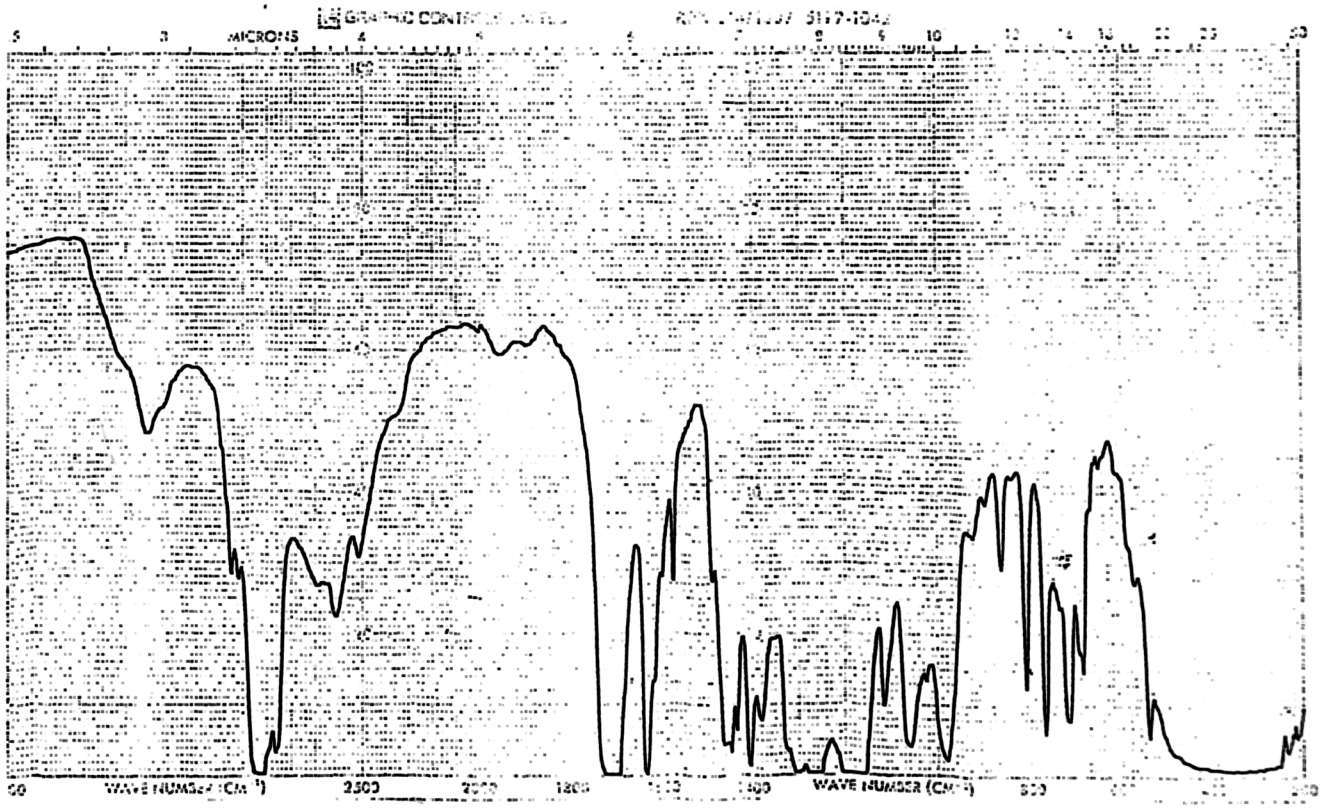


Fig 10.9 IR Spectrum of Cinnamoylated HDDA + Benzoylperoxide after 20 passes under Colordry

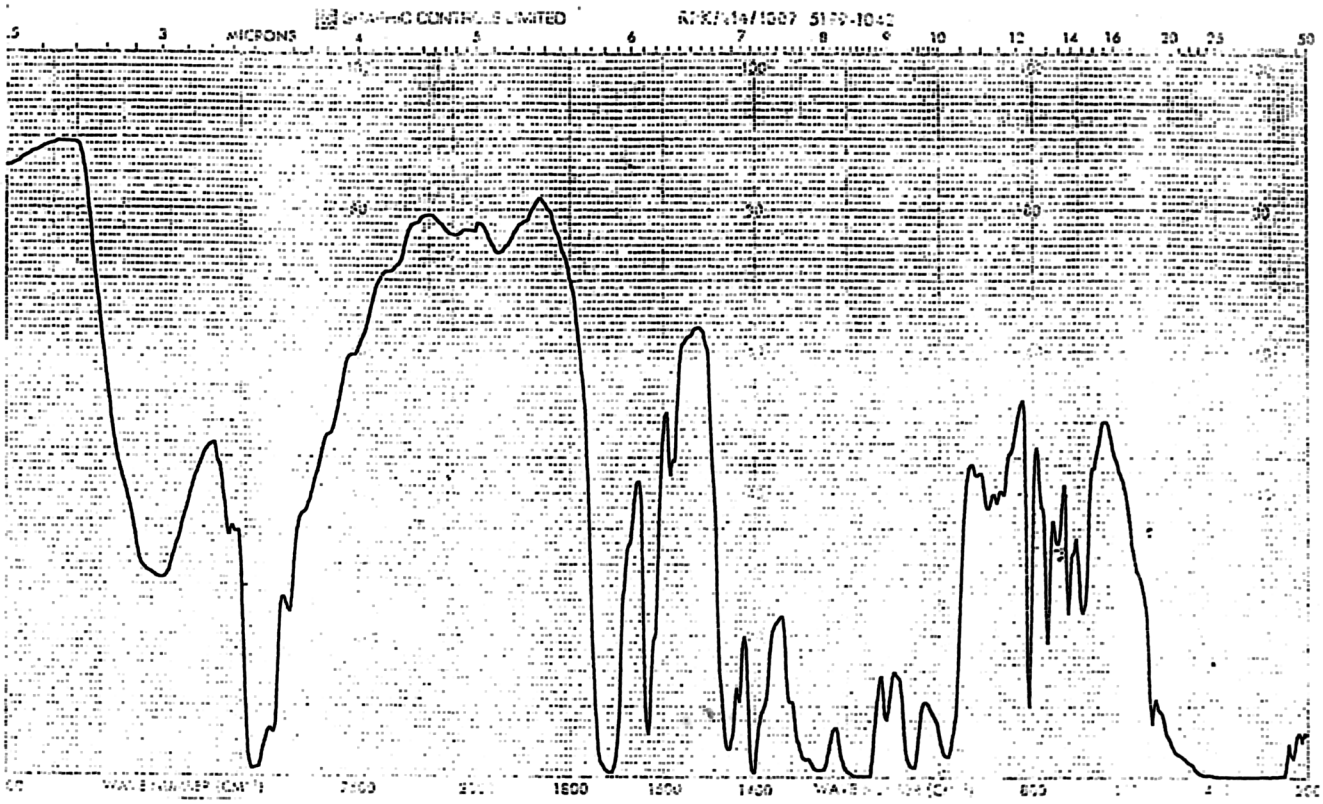


Fig 10.10 IR Spectrum of Cinnamoylated TMPTA + 10% of NMDEA + 2% Irg 907 before Irradiation

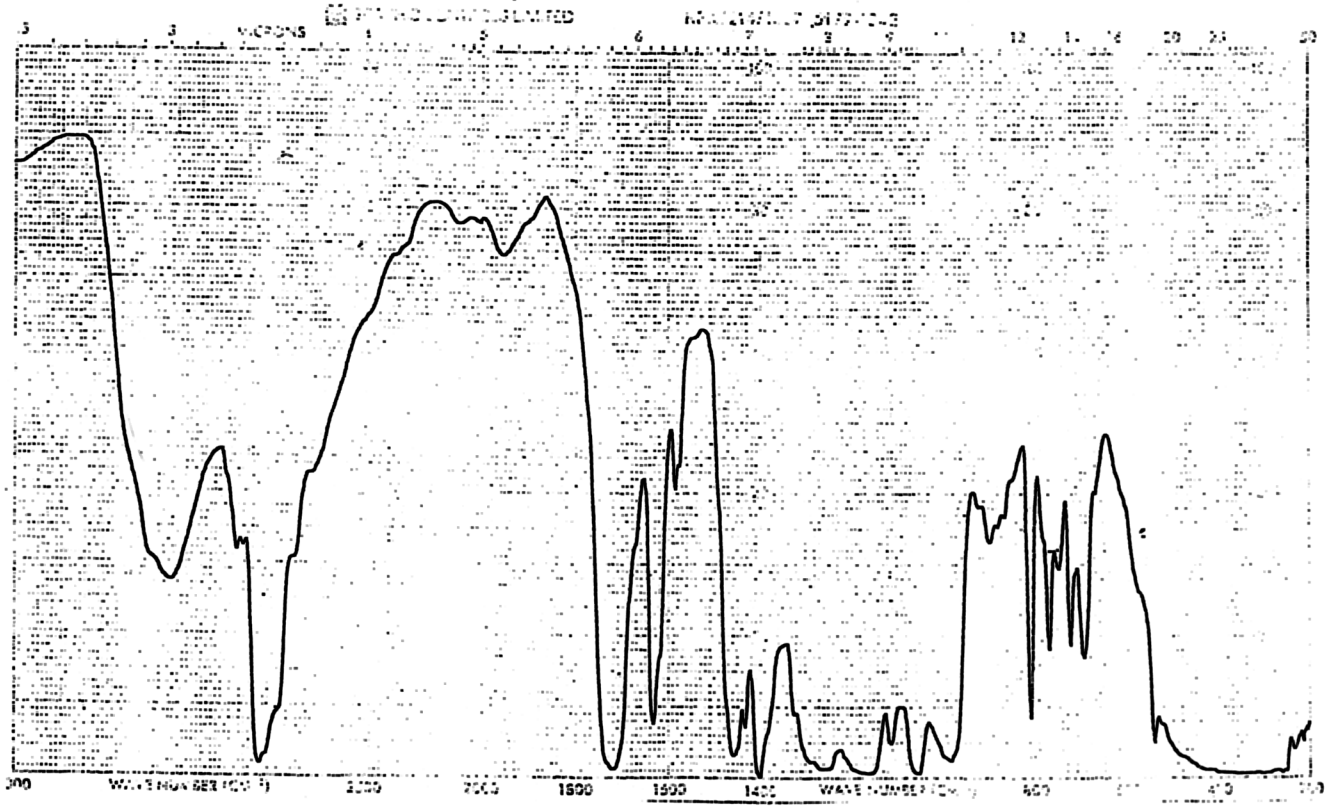


Fig 10.11 IR Spectrum of Cinnamoylated TMPTA + 10% of NMDEA + 2% of Irg 907 after 20 passes under Colordry

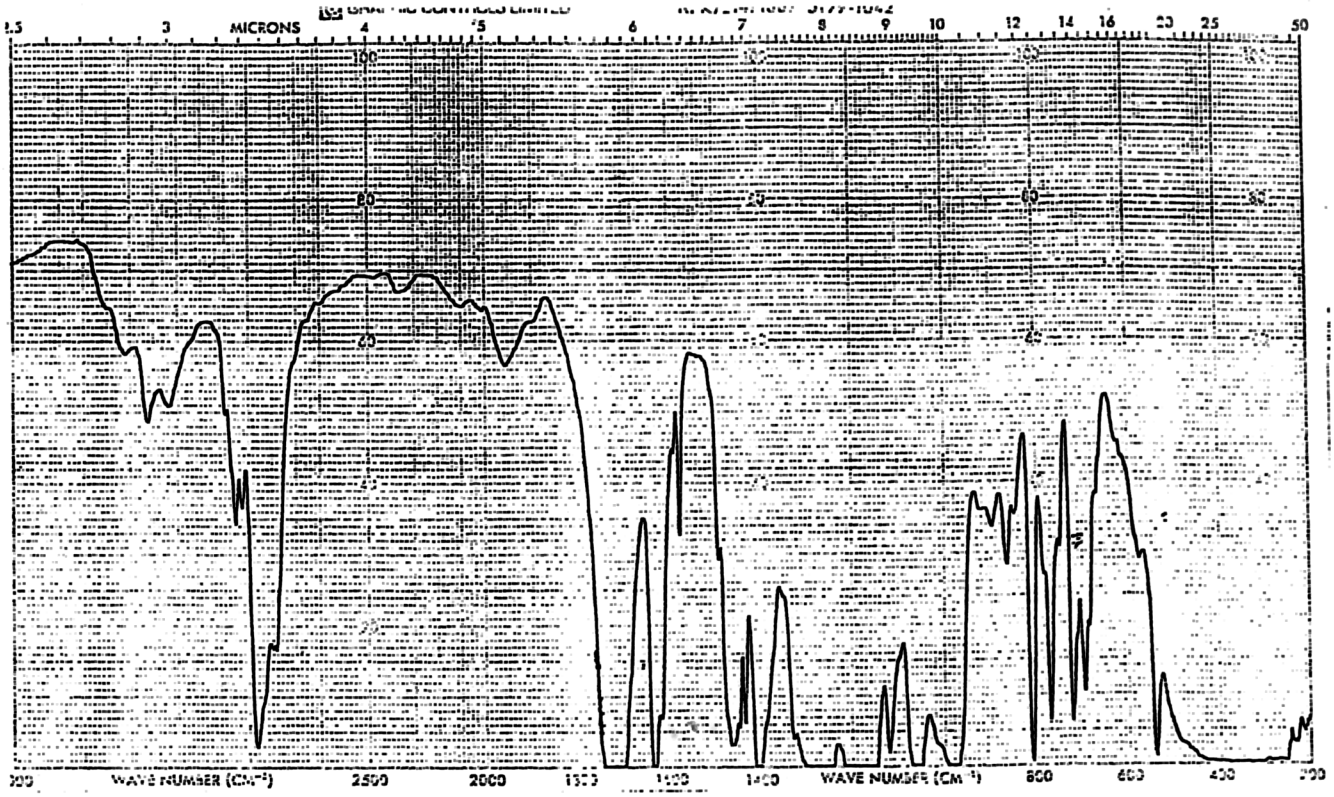


Fig 10.12 IR Spectrum of Cinnamoylated TMPTA before Irradiation

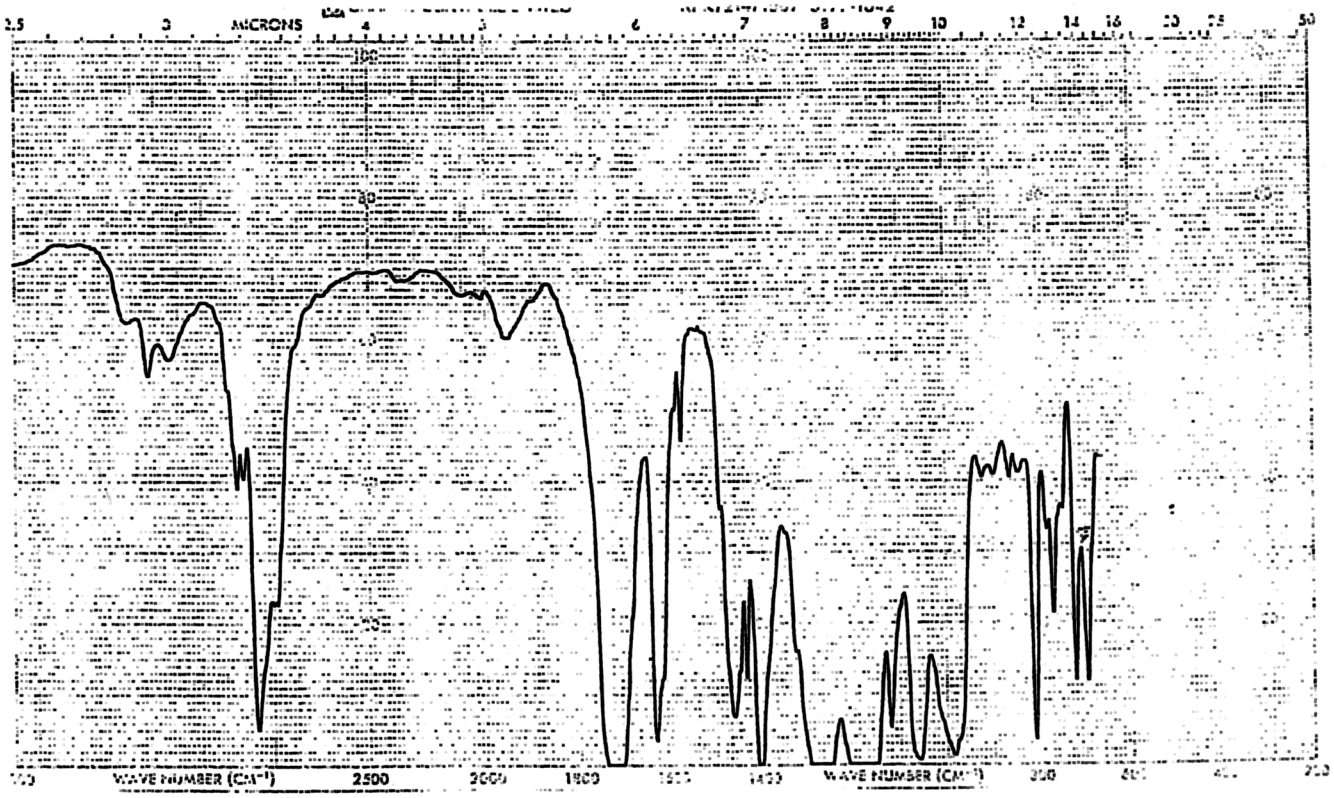


Fig 10.13 IR Spectrum of Cinnamoylated TMPTA after 20 passes under Colordry

Conversion percentage for Irg 907 + TMPTA was determined at around 35% but in the case of arylated TMPTA + Irg 907 and Arylated TMPTA + Irg 651 was not more than 2% (Figs. 10.5-13).

The lack of cure in these systems is puzzling. As the UV absorption spectra show, light will be absorbed by Irgacure 907 and to a lesser extent by Irg 651. Given the percentage of cinnamate groups present, no quenching of the triplets of Irg 651 should have occurred and possibly a relatively small amount of quenching of the triplets of Irg 907. It is unlikely therefore that the lack of cure is due to triplet quenching and the initiators are being decomposed as per normal. This leaves the possibility that the cinnamates are scavenging the benzoyl radicals. However acrylate-cinnamate mixtures can be polymerised thermally by such initiators of AIBN and benzoylperoxide. At present we can offer no explanation for the situation. If time had allowed we would have attempted to quantify the "quenching effect" that cinnamates have an acrylate polymerisation. The original idea of converting di and triacrylates into partially cinnamoylated derivatives to produce a dual cure system appears to be flawed. The only systems which are remotely similar and have been [40] reported to work are monoacrylated cinnamates which can be polymerised thermally to give a linear acrylate having pendant cinnamate groups.

EXPERIMENTAL

The Materials:

Trimethylolpropanetriacrylate, 1,6-hexanediol diacrylate, methylmethacrylate and pentaerythritol-triacrylate were obtained from Aldrich.

The method of arylation of acrylates is given in Chapter 2 .

Equipment:

The information about Real Time Infrared Spectroscopy is given in detail in Chapter 4.

IR + Colordry:

The samples were coated as a film on a NaCl plate using 24 KBar and cured under Colordry using a 100w (per inch) medium pressure mercury lamp and tested with a Perkin Elmer IR Spectrometer No. 599.

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